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by

DANIAL JOHN HEANEY

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Noorallah G. Juma

Date June 13, 1985

This thesis is dedicated
with love to my Dad

Abstract

The cycling of N has been extensively studied in agricultural soils during the growing season. The growing season is of short duration on the Canadian prairies. Therefore, research on the N cycle in prairie soils must be expanded to include the remainder of the year. Included within this latter period is the winter, when soils are frozen and their chemical, physical, and biological properties are different from the non-frozen phase. The purpose of this study was to examine the N cycle from fall through spring in three Black Chernozemic and one Gray Luvisolic soil located in central Alberta. Particular emphasis was placed on processes affecting mineral-N from late fall when the soil starts to freeze to the post thaw period immediately prior to seeding in the spring.

Four field experiments were conducted over the winters of 1980-81 and 1981-82. The first experiment of this series examined four soils for net changes in mineral-N levels in the top 60 cm of the profile. The remaining three experiments employed ^{15}N to trace N flow through the soil system. In two of the ^{15}N experiments, comparisons were made between fallow and stubble systems and residue amended *versus* non-amended systems. The remaining experiment investigated the overwinter release of N immobilized within the organic-N fraction.

Results showed that the processes affecting the mineral-N pool are active throughout the period when soils lie uncropped. Flow of N into the mineral-N pool was greatest during the fall-winter and winter-spring transitions and occurred mainly through biological processes. Non-biological release of N through physical and/or chemical mechanisms supplemented biological processes in mid-winter when the soil was frozen. Losses and redistribution of ^{15}N from the mineral-N pool occurred through immobilization, leaching, and denitrification. Redistribution of ^{15}N by immobilization in the organic-N fraction and leaching down the profile did not constitute a loss from the rooting zone for most crops and were considered as temporary losses only. Losses attributed to denitrification were greatest during the late fall and the winter-spring transition. Smaller losses occurred during the winter when the soils were frozen. During 1980-81, comparison of fallow *versus* stubble soils with above ground residues removed showed that denitrification losses between October and May were greater under stubble. Stubble soils, compared under residue amended and non-amended regimes the following year (1981-82), followed a different trend. Recovery in May of ^{15}N applied to the soils as NO_3^- November was increased by incorporation of residues, mainly due to an increase in immobilization of the label.

The major finding of this study was that the flow of N through the plant available pool is continuous throughout the year. Of particular interest from an agronomic standpoint, is the amount of N lost from agricultural soils outside the growing season. The present study suggests that overwinter N loss may be considerable and denitrification outside the growing season may make a substantial contribution to the declining fertility of soils in central Alberta.

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7

I. INTRODUCTION

Since prairie soils were first broken there has been a continual decline in their organic matter content and an accompanying loss of soil nitrogen (Campbell *et al.*, 1976). As a result, the original high fertility of prairie soils has been substantially reduced. The loss of nitrogen—only 60% of which may be attributed to crop removal (Campbell *et al.*, 1980)—has resulted in an increased reliance on nitrogen fertilizers by western Canadian farmers. For example, during the period 1958 to 1968, nitrogen fertilizer consumption in Alberta increased thirty fold, from 7,100 to 91,400 Mg (Beaton, 1980). The inconvience of handling large fertilizer applications during seeding operations in the spring led to the widespread practice of applying nitrogen fertilizers in the fall. This practice is based on the assumption that the severity of the prairie winter renders soils inactive, permitting fall-applied nitrogen to overwinter with minimum loss. In the early 1970's researchers began to question this premise. Leitch and Nyborg (1972) found that plots receiving fall applications of nitrogen were often outyielded by plots fertilized in the spring. Further work by Malhi (1978) with ^{15}N enriched fertilizers indicated that substantial and irrecoverable losses of fall-applied nitrogen occurred over the winter, if it was applied as NO_3.

Results from winter sampling studies suggested that overwinter losses were not confined to soils receiving fall inputs of fertilizer nitrogen. Changes in the native mineral-N levels of a Brown Chernozem of southern Saskatchewan (Campbell *et al.* 1970b) and Black Chernozems and Gray Luvisols of central Alberta (Malhi 1978) were also noted between fall and spring.

By the late 1970's, it was evident that soil mineral-N levels were not static over the winter; however, the magnitude of changes and the processes involved were poorly understood. Also the contribution of these overwinter changes to nitrogen loss from the soil system and declining fertility had not been quantified.

The objectives of the present study were:

1. To measure mineral-N levels between fall and spring by periodic sampling of three Black Chernozemic and a Gray Luvisolic soil located in central Alberta.

2. To describe the processes of gain and loss affecting the mineral-N pool between fall and spring in a Black Chernozemic and a Gray Luvisolic soil.

3. To partition the amounts of N lost from the mineral-N pool between potential loss mechanisms and to determine the effects of added crop residues on this partitioning.

II. LITERATURE REVIEW

Research into the soil N cycle has mainly dealt with N behavior in the active temperature range (i.e. 5-35°C). The results of such studies are applicable to soil N dynamics during the growing season. The subject of this study is the behavior of soil N during the remainder of the year, including the winter. The chemistry, physics, and biology of frozen soils differs in many aspects from the non-frozen phase. Therefore, it is important to review some of the differences between frozen and non-frozen soils in conjunction with soil nitrogen processes.

The separate subcycles of the soil N cycle interface within the mineral-N pool. The processes which link the separate subcycles to the mineral-N pool can be divided into three categories: chemical, physical, and biological.

A. PHYSICAL AND CHEMICAL STATE OF SOILS IN WINTER

Soil physicists and engineers have studied frozen soils for decades. As a result, the properties of frozen soils as a construction material and certain processes pertinent to their interests, such as frost heave, are relatively well understood. The study of frozen soils as an integral part of ecological systems is in its infancy. The term frozen soil is misleading. Soils may be subjected to subzero temperatures and contain frozen water, but within the temperature ranges to which soils are normally subjected to in the field they are never completely frozen. Soils are never frozen in the sense that chemical, physical and possibly biochemical activity ceases completely. Which processes are active and the rate at which they proceed is at present poorly understood, therefore, only a rudimentary description of the chemical and physical state of frozen soil is possible.

Temperature regime of soils in winter

Soil temperature on the Canadian prairies follows the same seasonal cycle as air temperature; however, the larger thermal mass of soil considerably reduces the amplitude of the cycles. The dampening effect can best be expressed as cooler in summer, warmer in winter. Bilello *et al.* (1970), working in Alaska, compared air temperature against soil temperature at a depth of 1 cm between October and May. They calculated a mean difference of 12.3°C. Judge (1973) used meterological data from across Canada to calculate the difference in winter between air and soil temperature at a depth of 2.5 cm. He reported that on the average soils were 3.3°C warmer than air.

Berry (1981), in a recent review, concluded that a large part of the difference between soil and air temperature in winter is due to snow cover. Snow reflects incoming short wavelength radiation and thus prevents heat gain by the soil. It also blocks the escape of long wavelength energy reradiated by soil and insulates against convective heat loss. The insulating properties outweigh the reflective properties and can maintain soils under snow cover well above subzero air temperatures. Potter (1958) measured snowpack depth in relation to soil temperature and found that once a snow depth of 30 cm was surpassed the soil temperature in the surface layer seldom fell below -2°C. Bleak (1970) made similar observations in Colorado, reporting that the surface 1 cm of soil under snow cover remained between -2 and 2°C regardless of ambient air temperature.

Moisture regime of soils in winter

During the process of soil freezing, ice tends to form in a pure state. Soluble impurities are excluded from the growing ice crystals, leading to the formation of a concentrated soil solution with a depressed freezing point (Miller, 1980) which collects at the interface of ice crystals and soil particles (Miller *et al.*, 1960). Unfrozen soil solution can also exist in soils at temperatures below 0°C in association with soil colloids. For example, Murrman *et al.* (1968) demonstrated that unfrozen moisture films remained in the interlamellar regions of bentonite at

-15°C. The amount of the unfrozen soil solution associated with ice crystals is a function of soil moisture at the time of freezing while the unfrozen soil solution associated with colloidal material is controlled by intrinsic soil parameters, most importantly specific surface area (Tice *et al.*, 1978). Nersesova and Tsytovich (1963) quantified the relationship between specific surface area, expressed as a function of texture with modification for clay mineralogy, and unfrozen water. In their study, the unfrozen portion of total soil moisture at -1 to -2°C ranged from 0.5% in coarse sands to 15-25% in clay soils dominated by montmorillonite.

Increases in the concentration of the soil solution caused by the exclusion of solutes as ice forms are difficult to measure. The existence of such a process has been demonstrated in bulk solutions of NaCl (Terwilliger and Dizio, 1970) and $CaCO_3$ (Hallet, 1976). Differences in the geometry of the soil matrix alters the ratio of frozen to unfrozen water in soils with the same unfrozen solution concentration (Hallet, 1978). As a result, the relationships between concentration, temperature, and frozen to unfrozen water determined in bulk solution studies cannot be extrapolated to soils in the field. Methods for measuring the effect of soil freezing on the concentration of the soil solution are still under development. In the absence of experimental data, Hallet (1978) postulated that exclusion of solutes could lead to a 50 fold rise in the concentration of the soil solution.

Moisture movement within a frozen soil can be greatly impeded by ice crystals which disrupt the continuity of the soil pores. Williams and Burt (1974) measured hydraulic conductivity over a range of subzero temperatures and found that at the same initial moisture content translocation of moisture declined with decreasing temperature. Pelton *et al.* (1967) measured hydraulic conductivity at a constant temperature while initial moisture content was varied. Their results suggested that hydraulic conductivity was a function of the initial moisture content and that at pre-freeze moisture contents approaching field capacity, soils were virtually impermeable. Both studies indicated an inverse relationship exists between ice content and the rate of solution flow through the soil matrix.

Effects of ice formation on reaction kinetics

Chemical and biochemical activity in soils are strongly affected by soil temperature. For many reactions, the relationship between temperature and reaction rate can be described by the Arrhenius approximation of the rate constant k:

$$k = Ae^{-Ea/RT} \tag{1}$$

Which may be transformed logarithmically to yield the function:

$$\log k = \log A - Ea/2.303RT \tag{2}$$

Where A is the reaction constant (1/sec), Ea is the activation energy (J mol^{-1}), R is the molar gas constant (8.3143 J $^0K^{-1}$ mol^{-1}), and T is the temperature (^0K).

If a simple hypothetical one step reaction is considered, for example:

$$X + Y \rightarrow XY \tag{3}$$

where X and Y are the reactants and XY the product. The initial rate of product appearance is given by the equation:

$$XY = k[X][Y] \tag{4}$$

The reaction rate constant (k) can be calculated from equation (2) provided the temperature and constants are known, and the reaction rate from equation (4). For example, assuming the following temperature and values of the constants for hypothetical reaction (3):

A = 5×10^{10} sec^{-1}

Ea = 8×10^4 J mol^{-1}

T = 273°K (0°C)

R = 8.3143 J $^0K^{-1}$ mol^{-1}

[X] = 2 μM

[Y] = 2 μM

then the rate constant, from equation (2) would be 2.47×10^{-5} sec^{-1} and the initial rate of product appearance would be 9.88×10^{-5} μM/sec.

Now consider the special case of a soil freezing. Assume a clay textured soil in which at -2°C, 20% of the water remains unfrozen (Nersesova and Tsytovich, 1963). A five fold increase in the concentration of X and Y occurs as a result of the 2°C temperature change. The rate constant, from equation (2), becomes 1.91 x 10^{-5} sec^{-1}, and the concentration of X and Y is increased to 10 μM. The new rate of produce appearance, from equation (4), is 1.91 x 10^{-3} μM sec^{-1}, an nineteen fold increase in reaction rate.

The simple model used above could be adapted to cover more complex chemical reactions and may also apply to first order or greater than first order biochemical reactions. Based on the above discussion, an increase in reaction rate as the soil freezes would be expected for those reactions governed by kinetics of the first order or higher.

B. BIOLOGICAL PROCESSES

Mineralization and Immobilization

Mineralization and immobilization are deemed the most important processes controlling the size and turnover of the mineral-N pool. Roswall (1976) calculated that on a global scale 95% of terrestrial N cycling occurs through mineralization/immobilization turnover (MIT), while only 5% interacts with the hydrosphere and atmosphere. McGill *et al.* (1981) have described the two processes as concurrent and opposing with respect to the level of mineral-N in a soil. Thus, the size of the mineral-N pool can be viewed as a reflection of the balance between mineralization and immobilization.

Phase concept of soil N

Since mineralization involves release of N bonded to organic C, it has been proposed that mineralization is a by-product of the microbial search for C in C limited systems (McGill *et al.*, 1973, 1975, 1981). The availability of soil C as a substrate for microbes follows a gradient from active to passive. Nitrogen associated with C follows a similar gradient. At present organic-N is viewed as existing, based on ease of mineralization, in four phases

(Jansson and Persson, 1982). The most stable phase has been called the passive fraction and has been defined in the laboratory as the fraction remaining after hydrolysis with alkaline reagents (Campbell, 1978). The mean residence time of N contained in the passive fraction, upwards of 100 years, has been determined by ^{14}C dating (Campbell *et al.* 1967; Jenkinson and Rayner, 1977; Paul, 1970). The organic-N compounds forming the passive fraction are, either by their chemical nature or physical location, excluded from the mainstream of MIT.

The remaining three phases of organic-N are the living biomass, fresh debris, and a stabilized fraction. The living biomass has been estimated to contain, depending on the type of soil, from 4 to 10% of total organic-N (Anderson and Domsch, 1978a,b; Jenkinson, 1966; Jenkinson and Powlson, 1976; Paul and Juma, 1981). While this is a small fraction of total organic-N, it is an important source of mineral-N. Campbell (1978), in a review of several authors' work, estimated that more than half of the N mineralized comes from biomass. Paul and Juma (1981) found, using a ^{15}N tracers and the fumigation technique for estimating biomass, that biomass N is the most rapidly cycling portion of organic-N. The process through which biomass N is mineralized have not been fully explained. It has been proposed by Monreal and McGill (1981) and McGill *et al.* (1981) that autolysis of cells and/or grazing of biomass by subsequent populations of soil micro- and mesofauna are the processes responsible.

Organic-N contained in fresh debris forms a second highly active phase (Fried *et al.*, 1975; Jenkinson, 1966; Paul and Juma, 1981). Paul and Juma (1981) found in a Chernozemic soil labelled with ^{15}N that mineralization from fresh debris was roughly equal to mineralization from biomass. Together these two phases contributed 60% of the nitrogen mineralized over a 12 week incubation. They calculated, by difference, that the remaining 40% of N mineralized arose largely from a stabilized fraction characterized by a half-life of 27 years. A similar fraction has been described by Campbell *et al.* (1967).

In summary of the four phases of soil organic-N, the passive phase, while containing the bulk of organic-N, has very little influence on the short term dynamics of the mineral-N pool. Existing data suggests that mineralized N arises from three active phases—biomass, fresh debris, and stabilized—in roughly equal proportions.

C:N ratio and MIT balance

Mineral nitrogen is converted to the organic-N fraction through immobilization in biomass. Biomass growth is often energy limited (Campbell, 1978); consequently, energy or available C is a major control on the immobilization rate. The balance between immobilization and mineralization is controlled by the C:N ratio of utilizable substrate. High C:N ratio substrates do not provide sufficient N to satisfy biomass requirements. The deficit is made up by drawing from the mineral-N pool resulting in net immobilization. When low C:N energy sources are used the excess of N above biomass requirements is released and accumulates as mineralized N. The average deflection point, delineating between net immobilization and net mineralization, occurs when substrates have a C:N ratio of approximately 25:1 (Iritani and Arnold, 1960; Jansson and Persson, 1982).

Microbial preference for NH_4^+

There is evidence that soil biomass prefers NH_4^+ to NO_3^- (Gainey, 1936; Jansson, 1958, 1971). Paul and van Veen (1979) suggested that the consequence of the microbial preference for NH_4^+ may be removal of NO_3^- from the mainstream of MIT. Campbell (1978) generally agreed with this hypothesis but points out that the heterogeneous nature of soil microflora ensures some NO_3^- immobilization occurs at all times. Care must therefore be exercised in interpreting results based on the immobilization of singular addition of NH_4^+ or NO_3^-. Additions of NH_4^+ may lead to overestimates of the turnover of the mineral-N pool while the converse may prove true when basing turnover solely on NO_3^- immobilization.

Temperature and moisture

Soil temperature and moisture exert strong environmental control over immobilization and mineralization processes. As temperature increases towards the optimum and moisture content approach field capacity, the rate of the two processes increases (Alexander, 1977). Stanford *et al*. (1973) reported that the mineralization rate rises exponentially between 5° and 35°C. Kai *et al*. (1969) found immobilization rates also increased as an exponential function between 10° and 40°C.

Temperature affects the rate but not the quantity of N immobilized. Kai *et al*. (1969) showed that the initial rate of immobilization at 10°C was approximately 25% of the rate at 40°C but more N was immobilized over a one week period at the lower temperature. Analagous findings were reported with respect to C mineralization and uptake by Sorensen (1981). In his study, short term carbon utilization dropped dramatically with temperature but over the long term the total amount of C used was independent of temperature.

Data on changes in the balance between immobilization and mineralization in response to temperature are scanty and contradictory. Kai *et al*. (1969) reported that as temperature declined immobilization rates declined more slowly than mineralization rates. Their data suggested that the balance shifts towards immobilization as temperature declines. Tison and Pope (1980) found that movement away from optimum temperature shifted C utilization away from uptake towards mineralization. Assuming N behaves in a similar manner (i.e. increased mineralization of C increases N mineralization) lower temperatures would be expected to favour mineralization over immobilization.

The foregoing laboratory studies illustrate general trends in the way immobilization and mineralization respond to temperature. However, care must be taken in using laboratory results obtained at constant temperature and moisture to explain *in situ* behavior of N. Temperatures in field soils follow a diurnal and seasonal cycle while mositure oscillates between wet and dry depending on the frequency and magnitude of precipitation events and the prevailing evapotranspiration rate. Investigations into the effects of changes in soil temperature and moisture on the N cycle have revealed that fluctuations in either are strong stimulators of MIT. Mineralization increases following wet-dry or freeze-thaw cycles (Mack, 1963; Hinman, 1970). Readily available microbial substrates are also know to increase following fluctuations in moisture and temperature..Hinman (1970) reported that soluble C levels increased in soils subjected to freeze-thaw cycles. Ivarson and Sowden (1970), in a similar experiment, classified the compounds responsible for the increase in soluble C as mainly amino sugars and amino acids.

The source of amino sugars and amino acids released following freeze-thaw cycles has not been determined. Alexander (1977) proposed that freeze-thaw or wet-dry cycles release organic C occluded in soil aggregates into the soluble C pool. Bryan (1971) and Soulides and Allison (1961) found that soil aggregates are disrupted by frost action. This supports Alexander's hypothesis. Contrary evidence can be assembled from the results of Campbell and his colleagues (Biederbeck and Campbell, 1971, 1973; Campbell and Biederbeck, 1972; Campbell *et al.*, 1970, 1971). In their studies, a variety of fluctuations in soil temperature and moisture; including freeze-thaw, warm-cool and wet-dry cycles; were found to be injurious to soil flora. Their observations lead to the formation of a second hypothesis. The increase in soluble C and accompanying burst of N mineralization following fluctuations in temperature or moisture are due to a release of N from the killed biomass. The correctness of either hypothesis is not implied by the present author nor is there any evidence that these two possible mechanisms of mineralization are mutually exclusive. One might speculate that under fluctuating conditions release of compounds containing mineralizable N into the soluble pool takes place through a mixture of both mechanisms. At present this would appear to be the most satisfactory explanation of the available data.

Mineralization and immobilization in frozen soils

Increases in the mineral-N pool of frozen soils have been previously reported by Campbell *et al.* (1970), Campbell and Biederbeck (1981), and Malhi (1978). The data obtained in their studies does not permit direct isolation of the mechanisms responsible for the accumulation of mineral-N but there is circumstantial evidence showing that mineralization occurs. Campbell and Biederbeck (1982) showed that soil bacterial populations are not static over the winter but decline as the soil freezes and then recover to high levels, exceeding summer maxima, once the soil system stabilizes in the frozen state. These results suggest that a large viable and potentially active microbial populations exist in frozen soils. The activity of such populations could conceivably, even at quite low rates, mineralize considerable amounts of N over the winter. Rice *et al.* (1984) pointed out that biological activity is not stopped by temperature below 0°C *per se* but is controlled ultimately by the liquid water content. A portion of the soil water remains in the liquid state at temperatures well below 0°C (Miller *et al.*, 1960; Murrman *et al.*, 1968; Tice *et al.*, 1978). Assuming that the temperature response curves for nitrogen mineralization can be extrapolated downward to -5°C, the mineralization rates reported by Kai *et al.* (1969) and Stanford *et al.* (1973) would convert to one eighth of those reported at 25°C. Nitrogen mineralized during the four to five months during which the soil is frozen would then be roughly equivalent to the amount mineralized during two to three weeks during the summer.

Biederbeck and Campbell (1982) did not explore whether or not the large populations found in frozen soils were composed of the same species found during warmer portions of the year. Is there a shift in the microbial suite from mesophylic to psycrophilic species. True psychrophiles, organisms which exihibit maximum rates of growth at temperatures below 15°C, are rare in soil. Most microbes capable of low temperature growth are actually cold tolerant mesophiles (Alexander, 1977). Nelson (1977) reported that bacteria isolated from high arctic soils, while capable of growth at -3°C, were in fact mesophiles with temperature optima in the 25 to 30°C range.

Further circumstantial evidence supporting biological mineralization at sub-zero temperatures can be found in a study by Bleak (1970). He reported extensive losses of plant litter placed in mesh bags on the soil surface and concluded that biological decomposition proceeded throughout the winter. His conclusion was based on reductions in the weight and changes in the visible appearance of the residues, which are not direct measurements of biomass activity. Respiration rates have not been measured in frozen soils; consequently, the activity of microbial populations and the accompanying MIT of N remains largely a matter of speculation.

Mineralization by exocellular enzymes

Campbell *et al*. (1971) proposed that biochemical mineralization in frozen soils might proceed through residual or exocellular enzyme activity without being associated with an active biomass. Exocellular urease activity has been detected in frozen soils to -10°C (Bremner and Zantua, 1975). Ladd and Jackson (1982), in a recent review, reported exocellular activity for a range of enzymes involved in ammonification including proteinases, amidohydrolases and ureases.

Exocellular enzymes are believed to be bound to porous matrices in the soil and generally exhibit a lower specific activity than their free counterparts. Engasser and Horvarth (1974a,b,c) have postulated that the reduced activity of bound enzymes is in part due to slow diffusion of the substrate through the binding matrix. The concentration of the substrate in the microenvironment of the binding matrix is thought to be lower than that of the bulk soil solution. As the soil freezes the increase in the concentration of the soil solution should theortically raise the rate of substrate diffusion to the catalytic surface. The rate at which nitrogen containing organic compounds are degraded by exocellular enzymes should also increase. Therefore, soils in the upper temperature range of the frozen phase might be expected to mineralize nitrogen more rapidly through exocellular pathways than soils at temperatures just above freezing.

Nitrification

Ammonium is strongly retained in soils through adsorption on the surface of negatively charged colloids. Nitrate, on the other hand, is highly mobile and subject to removal from soils by leaching and denitrification. The transformation of NH_4^+ to NO_3^- through nitrification is thus an important step linking the soil nitrogen cycle to the atmosphere and hydrosphere.

Microbiology

Unlike mineralization and immobilization, nitrification is carried out by a very limited number of soil organisms. Schmidt (1982) points out that numerous reports of heterotrophic nitrifiers exist in the literature (cf. Focht and Verstraete, 1972; Jensen, 1951; Schmidt, 1954) but only chemoautotrophs of the family *Nitrobacteriaceae* have actually been shown to nitrify in field soils. Within this family, nitrification appears to be dominated by two genera: *Nitrosomonas* oxidizing NH_4^+ to NO_2^- and *Nitrobacter* completing the oxidation of NO_2^- to NO_3^- (Alexander, 1977). The oxidation of NH_4^+ can be mediated to a lesser extent by species of other genera including *Nitrosococcus*, *Nitrosospira*, and *Nitrosolobus* (Schmidt, 1982). It was originally thought that a single species would competitively exclude all other species and form a homogenous ammonium oxidizing population (McLaren and Ardakani, 1972). Belser and Schmidt (1978) have to some extent refuted this idea. They found that the ammonium oxidizing community in soils was diversified with species of several genera present.

Substrate control

McClaren (1971) proposed that nitrification is most commonly limited by low concentrations of NH_4^+. Campbell (1978) supports this view and forwarded the idea that ammonium oxidizers compete rather poorly with the heterotrophic biomass for available NH_4^+. Lack of NH_4^+ may inhibit the growth of ammonium oxidizers, but there is evidence that the inhibiton is not passed down the nitrification pathway to the nitrite oxidizers. Volz *et al.* (1975) proposed that nitrite oxidizers and nitrate reducers (NO_3^- to NO_2^-) form an internal cycle feeding on itself. Belser (1977) found that the nitrite oxidizing populations in the soils he studied were at times an order of magnitude larger than those of ammonium oxidizers and their growth could not be supported by NO_2^- arising from the oxidization of mineralized NH_4^+ alone.

Effects of temperature on nitrification

Further limitations are placed on nitrification by soil temperature. Reported temperature optima for nitrification in temperate soils varies from 20°C (Malhi and McGill, 1982), 25 to 27°C (Justice and Smith, 1962; Waksman and Madock, 1937) to 30 to 32°C (Fisher and Parks, 1958; Anderson and Boswell, 1964; Kowalenko and Cameron, 1976). The lower temperature limit of nitrification were originally determined to lie between 1 and 2°C (Frederick, 1956 and Sabey *et al.*, 1956). Results of a study conducted in Alberta by Malhi and McGill (1982) indicate that nitrification proceeds at soil temperatures as low as -4°C.

Earlier researchers (Anderson and Purves, 1955; Ferederick, 1957) concluded that the variation in the temperature range over which nitrification occurs in different soils was a function of the size of the initial nitrifying population. Recently, Malhi and McGill (1982) have shown that the range and optimum temperature for nitrification is climatically determined and can be correlated to a gradient of mean annual soil temperature. Rice *et al.* (1984) furthered the above work and found pyschrophilic nitrifiers, with temperature optima between 5 and 10°C, in a Gray Luvisolic soil. Consequently, nitrification at lower temperatures may involve a different suite of bacteria in terms of either species or variety than those found at higher temperatures.

Fluctuating temperatures appear to stimulate nitrification. Frederick (1956) found that the highest rate of nitrification was obtained by subjecting soil to cool-warm cycles oscillating between 7 and 15°C. Sabey *et al.* (1956) noticed that soils in the field tend to nitrify more rapidly than soils incubated in the laboratory at comparable but constant temperatures. Part of this difference may be attributable to the stimulating effects of fluctuating temperatures.

Nitrification rates at low temperatures have largely been calculated to describe overwinter nitrification of NH_4^+ based fertilizers. Page (1975) found that the response of nitrification to temperature could be effectively modelled in a sandy soil by using an oxidation rate at 0°C of 0.5 to 1.0% of added NH_4^+ per week and a Q_{10} of 2.1. Based on low temperature incubation studies, Rice *et al.* (1984) calculated that at addition rates of 50-200 kg N/ha, 18-20 kg N/ha would nitrify in Alberta's aerable Chernozemic and Luvisolic soils between October and May. Field measurements of overwinter nitrification in Alberta support slightly higher rates. Malhi and Nyborg (1979) reported that 16 kg N/ha out of 56 kg N/ha added as NH_4^+ was nitrified between late October and early March. A considerably shorter period than that used by Rice and his coworkers in their calculations. The rate at which nitrification occurs over the winter in the absence of fertilizer N has not been determined. However, based on the results of the fertilizer studies cited above, one may conclude that nitrification of native NH_4^+ proceeds throughout the winter.

There is some evidence in the literature that nitrification may be incomplete at low temperatures. Justice and Smith (1956) showed that nitrite oxidizing bacteria ceased their activities at 2°C but NH_4^+ oxidizers were active in the 0 to -2°C range. Similar findings were reported by Pang *et al.* (1977) who showed that NO_2^- tended to accumulate in soils as temperature decreased.

Effects of moisture on nitrification

Nitrification has been measured at moisture tensions ranging from 0 kPa (Dubey, 1968) to 1500 kPa (Dubey, 1968; Miller and Johnson, 1964). Maximum velocities have been recorded at tensions of 33 kPa (Justice and Smith, 1962) and 50 kPa (Miller and Johnson, 1964). It has been pointed out that nitrification rates decrease as the soil dries but recover rapidly when the soil is rewetted (Schmidt, 1982). This phenomenon appears to be a manifestation of the size of the nitrifying population and its ability to expand rapidly when moisture limitations are removed (MacDonald, 1979).

Biological Denitrification

Biological denitrification has been described by Firestone (1982) as the major pathway by which soil nitrogen returns to the atmosphere. Hauck (1981) estimated that denitrification losses averaged 25-30% of added fertilizer N, clearly marking denitrification as a major limitation on the efficient use of nitrogen in agricultural production. In addition, denitrification of fertilizer N may have serious environmental ramifications. Gaseous oxides of nitrogen produced through the process of denitrification may increase the rate of ozone destruction in the upper atmosphere (Sze and Rice, 1976). They may also promote the greenhouse effect (Wang *et al.*, 1976). The importance of agricultural and environmental concerns has stimulated a tremendous amount of research into the denitrification process in a wide variety of ecosystems. The biochemistry and physiology of the process, however, is not completely understood.

Denitrification pathway

The most commonly hypothesized pathway of N oxide reduction by denitrifying bacteria is given by Firestone (1982) and Knowles (1981) as:

$$\overset{(+5)}{NO_3^-} \rightarrow \overset{(+3)}{NO_2^-} \rightarrow \overset{(+2)}{NO} \rightarrow \overset{(+1)}{N_2O} \rightarrow \overset{(0)}{N_2}$$

While the complicity of NO_3^- and NO_2^- in the denitrification pathway has been extensively documented (c.f. Firestone, 1982), the role played by the gaseous oxides of nitrogen in the reaction sequence is not clear. Nitric oxide has been reported both as a free intermediate (Firestone, 1979) and as being an intermediate but not released during denitrification (St. John and Hollacher, 1977). Nitrous oxide is known to be evolved by denitrifying organisms (Coreau *et al.*, 1980; Hooper and Terry, 1979; Ryden *et al.*, 1979) especially when NO_3^- is present in large quantities (Blackmer and Bremner, 1978). The mechanisms through which N_2O arises has not been clearly determined. Hooper and Terry (1979) proposed that N_2O may arise from a pathway involving NH_2OH (hydroxylamine) as an intermediate, while Blackmer *et al.* (1980) suggested that N_2O was a product of NO_2^- reduction. The further reduction of N_2O to N_2 yields microbially available energy but there is evidence that N_2O alone cannot support microbial growth (Bryan, 1980).

The initial step in the denitrification pathway, the reduction of NO_3^- to NO_2^-, is believed to interact strongly with nitrification. Volz *et al.* (1975) proposed that NO_3^- reduction and NO_2^- oxidation form an internal self-sustaining cycle. An incubation study by Belser (1979), in which populations of nitrite oxidizing bacteria where found to be much larger than ammonium oxidizers, supports the hypothesis forwarded by Volz's group. The coupling of these two reactions, one aerobic, the other anaerobic, are thought to occur in adjacent microsites separated by an aerobic-anaerobic interface (Knowles, 1978).

Microbiology

It has been established that denitrification is carried out largely by facultative anaerobic bacteria from a wide range of soil genera (Firestone, 1982). Hall (1978) lists 73 genera of soil bacteria capable of catalyzing the first step of dissimilatory NO_3^- reduction (NO_3^- to NO_2^-), while Focht and Verstraete (1977) report 23 genera capable of reducing NO_3^- or NO_2^- to gaseous forms. It is not entirely clear which genera or species are the most important denitrifiers. The most commonly isolated ones are species of the genera ***Pseudomonas*** and ***Alcaligenes*** (Gamble *et al.*, 1977). Alexander (1977) estimated, based on a compilation of studies by other researchers, that species of the former genus account for 3 to 15% of soil bacteria while the latter accounts for 2 to 12%. Based on these ranges, denitrifying bacteria can be seen as forming a substantial portion of the microbial flora normally found in agricultural soils.

Soil carbon

The relationship between soil C and denitrification has been described with respect to both total C (Bremner and Shaw, 1958; McGarity, 1961; Stanford *et al*, 1975b) and indices of available C (Burford and Bremner, 1975; Monreal, 1983; Stanford *et al.*, 1975b). Total C levels in soil are directly related to the size of the microbial community (Alexander, 1977). Indices of available C are, on the other hand, thought to represent the reductive potential of a soil as it pertains to denitrification. Consequently, both population size and substrate supply have been implicated as important determinants of a soil's denitrification potential. Terry and Tate (1980) observed higher soluble C levels and denitrification rates on a cropped compared to a fallowed soil. They were unable to discern a relationship in their data between initial population size and the rate of NO_3^- disappearance. Rice *et al.* (1984), in a study of denitrification potentials in Chernozemic and Luvisolic soils, found that N_2O production was correlated to percent total C but not to water soluble C levels. Their results suggested that available energy was not limiting denitrification *per se* and differences between the eight soils were likely attributable to the size of the denitrifying population. The issue raised by these apparently contradictory results is not so much which factor, initial population size or substrate supply, limits denitrification, but under which conditions one or the other becomes the most limiting factor.

Effects of organic amendments

Studies into the effects of organic amendments on denitrification have produced contradictory but not inexplicable results. Craswell (1978) reported that additions of straw increased immobilization and thereby prevented denitrification. Additions of manure on the other hand have been found to greatly increase denitrification (Guenzi *et al.*, 1978). In the latter study, increased denitrification was attributed to high respiratory consumption of O_2 increasing the reductive potential at the microsites. To a certain extent the gulf between the dissimiliar findings reported in the preceeding studies has been bridged by Rolston *et al.* (1979). Rolston's group found that the denitrification rate was increased in amended compared to non-amended soils but was also accompanied by an increase in the immobilization rate. They suggested that organic amendments may stimulate short term denitrification but lower losses over the long term by immobilizing N in the organic-N pool.

Oxygen control

The synthesis and activity of the enzymes involved in denitrification is possible only under conditions of reduced O_2 availability (Firestone, 1982). In this sense, denitrification appears to be consistent with the generally observed preference of microbes for metabolic pathways with higher energy yields (Stouthamer, 1976). Details of the mechanism by which O_2 inhibits synthesis and activity are not known. However, mutants of *Pseudomonas aeruginosa* incapable of utilizing O_2 are able to reduce NO_3^- aerobically, suggesting that O_2 must replace NO_3^- as the terminal electron acceptor in order to inhibit denitrification (van Hartingsvelt and Stouthamer, 1974).

The effects of O_2 on enzymes other than nitrate reductase are not well understood. It is known that not all steps in the reduction chain are equally affected. Nitrate and nitrite reductases are functional at higher O_2 concentrations than the enzymes involved in the subsequent reduction of N_2O (Krul and Veeningen, 1977). This results in a proportional shift of denitrification's gaseous end products away from N_2 and towards N_2O as O_2 concentration increases (Knowles, 1981) and may be important in terms of the impact of denitrification on atmospheric chemistry.

Moisture content and bulk soil parameters

The diffusion of O_2 through water is considerably slower than through air; consequently, O_2 concentration and denitrification rates are largely controlled by soil moisture content (Firestone, 1982). Threshold moisture contents have been characterized by Bremner and Shaw (1958) and Nommik (1956) as 60% of maximum water holding capacity. While the above studies indicate that denitrification may take place in relatively dry soils, Pilot and Patrick (1972) found that it did not reach significant proportions until 86 to 89% of the pore volume was water filled (100% pore volume is equivalent to maximum water holding capacity). Ryden and Lund (1980) measured N_2O production over a range of soils and reported peak denitrification rates at moisture tensions close to saturation (5 to 10 kPa). Craswell and Martin (1975) found that ^{15}N enriched NO_3^- disappearance was not detectable over relatively long incubation periods in soils below saturation.

The variability of the results discussed above suggests that the interactions between moisture content, oxygen level and denitrification rate are complex and may be modified by secondary factors. Pilot and Patrick (1972) observed that denitrification commenced at lower moisture contents in fine textured compared to coarse textured soils. However, effects of texture alone do not account for all the variability reported in the relationship between moisture content and denitrification rate. Gilliam *et al.* (1978) measured denitrification rates over a range of soil textures and related the results to five additional soil variables: moisture content, moisture tension, redox potential, O_2 concentration, and hydraulic conductivity. All were found to be influential. Differences in denitrification rates, however, were only partially explained by their relationship to the variables measured. Gilliam's group concluded that microstructure and the conditions within the immediate environs of the denitrifying bacteria were the final determinants of denitrification rates.

Denitrification at microsites

The concept of anaerobic microsites has been developed to explain denitrification in aerobic soils. Greenwood (1961) postulated the existence of anaerobic conditions in the interior of soil crumbs greater than 3 mm in diameter. He later, based on the diffusional characteristics of O_2 through water, increased his estimate to 9mm (Greenwood, 1975).

Craswell and Martin (1975) formulated an active rather than a passive concept to explain the occurrence of denitrification at microsites. They proposed that anaerobiosis is a results of intense O_2 consumption on aggregate surfaces rather than slow diffusion to the interior. Following the active concept, the possible locations of anaerobic microsites within soils includes pockets within rapidly decomposing organic debris (Guenzi *et al.*, 1978), and the rhizospheres of actively respiring roots (Woldendorp, 1962).

Effects of depth on denitrification rates

Denitrification generally decreases with depth (Cho *et al.*, 1979; Khan and Moore, 1968). This trend reflects the distribution of organic matter in the soil profile (Firestone, 1982). Brar *et al.* (1978) measured the number of denitrifying organisms in soil profiles and found populations declined rapidly with distance from the surface. Similarly, Cho *et al.* (1979) described microbial activity (CO_2 production) and denitrification rate as an inverse exponential function of depth. Exceptions to the generally observed low rates of denitrification below the surface horizon have been observed in soils where subsurface C levels have been augmented by root exudate (Volz *et al.*, 1976) or leaching (Myers and McGarity, 1971, 1972).

Soil temperature

Denitrification rates are strongly affected by soil temperature. Stanford *et al.* (1975a) reported that the temperature response follows a classical Arrhenius relationship between 15 and 35°C with a Q_{10} of 2. Below 15°C denitrification rates decline rapidly and the Arrhenius equation does not apply (Cho *et al.*, 1979; Keeney *et al.*, 1979; Stanford *et al.*, 1975a). The lower temperature limits of denitrification in saturated soils has been reported, based on the results of incubation studies of several days duration, as 2°C (Bremner and Shaw, 1958), 3°C (Nommik, 1956) and 5°C (Bailey and Beauchamp, 1973). Stanford *et al.* (1975a) were able to detect denitrification at 0°C by using a relatively long incubation time, while Rice *et al.* (1984) detected denitrification in Chernozemic and Luvisolic soils at -4°C. This latter result suggests that denitrification might proceed throughout the winter in Alberta. Rice *et al.* (1984) pointed out that denitrification losses while detectable to -4°C were not likely to reach significant proportions in the short term until soil temperature rises above 3°C. An earlier study conducted on irrigated soils in Alberta reached similiar conclusions. Cho *et al.* (1979) used a threshold temperature for denitrification of 2.75°C in developing a model to describe denitrification losses on a year round basis. Based on their temperature response equations, denitrification could be expected to proceed at steadily declining rates through the late fall and early winter until it became negligible during mid-winter.

Bailey and Beauchamp (1973) showed that the conversion of NO_3^- to NO_2^- stops at a higher temperature than the subsequent reductions to gaseous forms. In the 2 to 5°C range the composition of evolved gases shifts away from N_2 towards NO. It has not been established whether this shift is due to differences in the temperature characteristics of the enzymes catalyzing the reduction of NO_2^-, NO and N_2O or indicates the activity of a chemical denitrification pathway, as proposed by Christianson and Cho (1983).

Interactions among temperature, moisture, and oxygen have been studied by Craswell (1978). He found that as temperature decreases a higher moisture content is necessary before denitrification will proceed. This may be due to the increased solubility of O_2 in cold water or decreased microbial respiration rates at low temperatures lowering O_2 consumption (Craswell, 1978; Firestone, 1982). The interaction of increased O_2 solubility and lower O_2 consumption may explain why denitrification, in soils incubated at one moisture content over a range of temperatures, is not described by the Arrhenius equation in the lower end of the temperature range.

C. PHYSICAL PROCESSES

Leaching

Leaching losses have not been studied extensively on the Canadian prairies. Based on limited data from Saskatchewan, Rennie *et al.* (1976) estimated that approximately 20% of the N lost since the onset of cultivation was attributable to leaching. The amount of N lost (approximately 600 kg N per cultivated hectare) is important in terms of agricultural production, representing the N requirement of from 8 to 12 years of cereal or oil seed crop production (Beaton, 1980).

Two major preconditions must be met before significant leaching losses will occur: the NO_3 content of the soil must be high and substantial water movement down the profile must take place in terms of both quantity and distance (Legg and Messinger, 1982). Dominant modifying factors include seasonal changes in the temperature, moisture, and hydraulic conductivity regime of the soil.

Temperature and moisture

On the prairies high evapotranspiration rates maintain cropped soils in a moisture deficit during the growing season. Leaching during the summer in soils under crop is unlikely. The opposite may be true of soils under fallow. Rennie *et al.* (1976) concluded that precipitation falling on fallow soils in Saskatchewan penetrates to a greater depth than on cropped soils. Their conclusion was based on differences in the distribution of NO_3 with depth under adjacent crop-fallow and continuously cropped sites. Similar observations were made in Manitoba soils by Michalyna (1959).

Outside the growing season, lower temperatures reduce evaporation. Transpiration ceases once the crop is removed and the moisture deficit may be reversed. Cameron *et al.* (1978), working with a sandy soil in Ontario, found that leaching was negligible under crop but added NO_3 was rapidly displaced down the profile by post harvest rains. In another study conducted on a fine sandy loam soil in Manitoba, spring applied NO_3 was retained in the top 30 cm through the summer. It moved below 120 cm during the subsequent fall and spring (Chang and Cho, 1974).

In addition to decreasing the evaporation rate, low temperatures decrease immobilization and may consequently increase the amount of NO_3 available for leaching (Khanna, 1981). While these circumstances may apply to NO_3 fertilizer additions, mineralization and nitrification are also slowed by cooler temperatures. It seems unlikely that the leaching of NO_3 in unfertilized soils would be significantly enhanced by decreased immobilization at lower temperatures.

Texture

The relationship between texture and leaching has not been rigorously tested on the Canadian prairies. Field-Ridley (1975) reported that NO_3^-, surface applied to clay and loam soils, did not move below 150 cm over a two year fallow period. Chang and Cho (1974) found the opposite to be true of NO_3^- applied to find sandy loam. Viewed together the results of these two studies suggest that short term leaching losses may generally be confined to coarse textured soils with high hydraulic conductivities.

Movement of NO_3^- in Response to Temperature Gradients

As soils freeze the temperature gradient established between the frost front and unfrozen soil below and the increased matric potential of the frozen soil, due to the removal of water from solution as ice, can induce a migration of moisture to the frost front (Miller, 1980). If this migration involves mass flow of liquid, then solutes, such as NO_3^-, can be carried upward and deposited at the frost front as the migrating water freezes.

There is some controversy regarding the phase in which moisture travels to the frost front. Kuzmak and Sereda (1957) found that in unsaturated sand columns subjected to a temperature gradient, moisture movement was due to vapour transfer alone and there was no movement of soluble salts toward the cooling front. Their study supported earlier reports that moisture migrates towards a cooling front as vapour and returns as liquid drawing solutes away from the cooling front (Gurr *et al.*, 1952). Dirksen and Miller (1966), working with fine textured soils, observed freezing induced moisture redistribution under less than saturated conditions. The magnitude of the moisture flux in their study was too large to be explained by vapour transfer alone. Similar findings were reported by Cassel *et al.* (1969). They proposed that both vapour and liquid transfer takes place as the soil freezes, with the balance between the two phases controlled by initial moisture content, soil texture, and the magnitude of the temperature gradient.

Surveying the literature leads to the conclusion that NO_3^- will migrate up the profile in response to the penetration of a frost front if certain preconditions are met. The preconditions were defined in a recent review of freezing phenomena in soils by Miller (1980). The soil must be above the moisture content at which liquid flow commences. There must be NO_3^- at lower depths in the profile and the freezing front must migrate downward relatively slowly, to permit time for a relatively large volume of solute bearing water to migrate towards the surface. If these three preconditions are met, then upward moisture movement may lead to an accumulation of NO_3^- in surface horizons as the soil freezes. Such an accumulation, however, may be somewhat ephemeral. Miller (1980) postulated that NO_3^- transferred upward to the frost front, travels back down the profile with the front and is eventually deposited below the zone of frost penetration.

Fixation and Release of NH_4^+

Ammonium present in the mineral-N pool consists of those NH_4^+ ions held in readily exchangeable sites on soil colloids. It represents only a small portion of the inorganic NH_4^+ held in soils. A much larger portion is held within the interlattice spaces of 2:1 clay minerals, where it remains comparatively non-exchangeable. The amount of NH_4^+ held in the non-exchangeable or fixed pool can be substantial. In surface horizons of soils on the Canadian prairies, from 7 to 14% of total-N may be present as non-exchangeable NH_4^+ (Hinman, 1964; Moore, 1965). The percentage increases to 20 to 50% in subsurface horizons.

The division of NH_4^+ into exchangeable and non-exchangeable pools does not accurately describe the retention of NH_4^+ by soil colloids (Nommik and Vahtras, 1982). A gradient of exchangeability exists, from readily exchangeable to non-exchangeable including a slowly or partially exchangeable pool. Both microbes and plants have an ability to extract NH_4^+ from fixed positions (Black and Waring, 1972; Blasco and Cornfield, 1966; Bower, 1951). However, most studies of non-exchangeable NH_4^+ fixation and subsequent extraction by plants or microbes involve preliminary additions of NH_4^+ in the laboratory or greenhouse. They may in consequence not accurately reflect the extent and manner in which native non-exchangeable NH_4^+ affects the dynamics of mineral-N in field soils.

Influence of environmental and soil factors

The ability of a soil to fix NH_4^+ appears to be an intrinsic property, dependent on the clay minerology of the soil in question (Nommik and Vathras, 1982). The amount and rate at which soils fix NH_4^+, on the other hand, is controlled by such soil and environmental variables as soil moisture, temperature, pH and the concentration of NH_4^+ in solution.

Generally, the amount of NH_4^+ fixed in a soil is higher at lower moisture contents. This trend may be due to increases in the concentration of solution NH_4^+ at lower moisture contents or, in the case of soils containing 2:1 clay minerals, because the clay lattice is contracted at lower moisture contents (Nommik and Vahtras, 1982). Drying of moist soils or alternate wet-dry cycles promotes NH_4^+ fixation. Blasco and Cornfield (1966) reported that oven drying at 100°C increased fixation capacity 12 fold over moist soil and that alternate wet-dry cycles were even more effective at promoting fixation, increasing NH_4^+ retention 16 fold. Results similar in nature but smaller in magnitude have been reported for soils dried or subjected to wet-dry cycles at lower temperatures (Black and Waring, 1972; Walsh and Murdock, 1960).

The effects of soil temperature on NH_4^+ fixation have not been extensively studied. Nommik (1957) found that a larger percentage of added NH_4^+ was fixed in short term experiments as soil temperature was increased from 0 to 60°C with soil moisture held constant.

Data concerning the effects of soil freezing on NH_4^+ fixation is confined to laboratory studies. Walsh and Murdock (1960) subjected soils amended with NH_4^+ to temperatures of -15°C for 5 days. Their results indicate that freezing approximately doubled the amount of NH_4^+ in the non-exchangeable pool. Similarily, Nommik (1965) showed that, in clay textured soils, the amount of fixed NH_4^+ increased by 10% following freezing at -17°C for 24 hours.

Nommik and Vahtras (1982) suggest that freezing dessicates soil through ice formation and consequently increases fixation by increasing the solution concentration of NH_4^+ and collapsing the clay lattices. There is indirect evidence in the literature that this phenomenon may not apply universally to all soils. The effects of freezing on non-exchangeable K^+, which is thought to behave in a manner analogous to NH_4^+, was investigated by Fine *et al.* (1940). They reported, in contrast to laboratory studies of NH_4^+ fixation, that K^+ was released from non-exchangeable position in two-thirds of the soils subjected to freeze-thaw cycles. The remaining third fixed K^+ under the same conditions. A later study confirmed that some soils release K^+ when frozen and then thawed (Graham and Lopez, 1969). The mechanism of K^+ release was not clear but Graham and Lopez (1969) thought that frost disruption of clay domains may be a factor in transforming K^+ from non-exchangeable to exchangeable form.

Raising NH_4^+ concentration increases the amount of NH_4^+ fixed in soils (Nommik and Vahtras, 1982; Nommik, 1965). Freezing the soil, hypothetically, increases the solution concentration of NH_4^+ and should promote fixation. The preceeding discussion on K^+ fixation under freeze-thaw conditions illustrates that not all soils are affected in the same way. The influence of freezing on fixation and release of non-exchangeable cations appears to be expressed through the interaction of several factors, including solution concentration, degree to which clay lattices collapse, and possible disruption of clay domains by ice formation. While data on the subject is scanty, it would seem likely that the response of soils to freezing, either to release or fix NH_4^+, is variable.

D. CHEMICAL PROCESSES

Chemodenitrification

Chemodenitrification, the reduction of NO_3^- to gaseous forms through purely chemical pathways, has received considerable attention in recent years (Chalk *et al.*, 1975; Christianson *et al.*, 1979; Court *et al.*, 1974; Smith and Chalk, 1979, 1980; Wetselaar *et al.*, 1972). Of particular interest with respect to frozen soils is the work by Christianson and Cho (1979, 1983). They observed that gaseous nitrogen losses from soils amended with ^{15}N enriched NO_2^- decline steadily with soil temperature until the soil freezes at approximately -2°C. Between -2 and -4°C evolution of gaseous nitrogen proceeds at rates approaching those measured at 20°C. Isotope analysis of the gases evolved suggested that NO_2^- was reduced through chemical reactions with soil organic matter rather than through biological denitrification.

The significance of chemodenitrification in frozen field soils remains a matter of speculation. Under conditions of moderate temperature and adequate moisture NO_2^- does not accumulate in soil (Alexander, 1977). This makes it difficult to extrapolate results using NO_2^- amended soils in the laboratory to field conditions. There is some data suggesting that nitrite oxidizing bacteria are less sensitive to low temperatures than ammonium oxidizers (Justice and Smith, 1962). Nitrite may, therefore, accumulate and chemodenitrification increase as soil temperatures decline in the fall. Malhi and McGill (1982) found no evidence of NO_2^- accumulation in incubation studies at low temperatures. However, that NO_2^- accumulation is prerequisite to appreciable chemodenitrification is questionable. Christianson and Cho (1979) reported that the reaction follows first order kinetics and calculated that the rate of NO_2^- loss was zero below 50-70 μg NO_2^--N/g. Their results are based on short term incubation studies and may be a reflection of detection limits imposed by the duration of the experiment rather than actual limitations due to concentration. Nelson and Bremner (1969) detected chemodenitrification at NO_2^- concentrations as low as 10 μg NO_2^--N/g. and found that as a proportion of the amount originally present more NO_2^- was lost at lower concentrations.

One can speculate that following NH_4^+ oxidation, NO_2^- is normally partitioned between further biological oxidation to NO_3^- and chemodenitrification. The losses observed during nitrification of NH_4^+ based fertilizers in well aerated soils, as reported for example by Bremner and Blackmer (1978), add validity to the preceeding hypothesis. However, the amount of native nitrogen lost through this mechanism in field soils, especially under favorable conditions such as when the soil is frozen, has yet to be determined.

III. METHODS AND MATERIALS

This study consisted of four field experiments conducted over the winters of 1980-81 and 1981-82:

i) Experiment 1980A : Changes in mineral-N levels between November and May.

ii) Experiment 1980B : Losses between November and May of native mineral-N.

iii) Experiment 1981A : Dynamics of soil N labelled with ^{15}N in the fall of the previous year.

iv) Experiment 1981B : Effects of barley residue on the dynamics of mineral-N between November and May.

A. SOILS

Four central Alberta soils were used in this study. Three of the soils, located near the towns of Olds, Ellerslie, and Calmar, were Black Chernozems of the Didsbury, Malmo, and Navarre series respectively. The fourth soil was a Gray Luvisol of the Breton series, located at the Breton plots. Soil characteristics and legal locations are presented in Table 1. Experiment 1980A was conducted at all four locations while Experiments 1980B, 1981A, and 1981B were carried out at Ellerslie and Breton. Level uniform sites were selected at each location. The sites were set away from tree lines and fences and had a recent history of cereal grain cropping with occasional summerfallowing.

Table 1. Characteristics of surface 15 cm of soils used

Soil	Legal location	Soil order	%OM	%N	pH	Bulk density	Texture
Breton fallow	SE-36-47-4-W5	Gray Luvisol	4.1	0.15	6.3	1.03	Clay loam
Didsbury fallow	NE-21-32-1-W5	Black Chernozem	11.4	0.46	6.4	0.97	Loam
Didsbury stubble	SE-21-32-1-W5	Black Chernozem	12.1	0.43	6.4	1.18	Clay loam
Malmo fallow	NE-20-51-24-W4	Black Chernozem	12.4	0.47	5.9	1.01	Clay loam
Malmo stubble	NE-20-51-24-W4	Black Chernozem	14.4	0.55	5.8	0.98	Clay loam
Navarre fallow	NE-25-49-28-W4	Black Chernozem	9.2	0.35	5.9	0.94	Silty clay loam
Navarre stubble	NE-25-49-28-W4	Black Chernozem	8.8	0.31	6.1	1.01	Silty clay

B. EXPERIMENTAL

Experiment 1980A

Plots (24 m by 6 m) were establish in three replicates during the fall of 1980 on adjacent stubble and fallow areas of the Didsbury, Malmo, and Navarre soils. On the Breton soil, plots were on fallow only. The plots were sampled in late fall, early winter, late winter and following the spring thaw. Eight to ten soil cores were obtained per plot at each sampling date. Each core was divided into sections corresponding to the 0-15, 15-30, and 30-60 cm depths. The sections were bulked by depth increment, mixed thoroughly, and a 1 kg sample removed for laboratory analysis. Samples were stored moist until such time, normally 12 to 24 hours after sampling, as a 30 g subsample could be removed for gravimetric determination of moisture content. Samples were then spread thinly to dry at room temperature. Air dry samples were ground to pass 2 mm in a roller mill. The ground soil was passed through a sample splitter and a 200 g sample withdrawn for NH_4^+ and NO_3^- analysis.

Additional bulk samples (approximately 5 kg in size) were obtained from each depth at the first sampling date. The bulk samples were air dried and ground to pass 2 mm. They were later used in the determination of soil characteristics.

Experiment 1980B

Experiment 1980B was set out as a modified complete block design on stubble and fallow areas of the Breton and Malmo soils. A total of 12 plots, divided into three blocks of four, were used on each stubble or fallow area. Each plot was contained within a wooden frame 100 x 100 x 15 cm (length x length x depth) set into the ground to a depth of 13 cm. In mid-October, the soil within each frame was removed to a depth of 13 cm and passed through a screen with 1 cm openings. On the stubble plots, loose surface straw was removed prior to excavation. Standing stubble screened out during the initial processing was reincorporated evenly throughout the soil. Two plots from each block were amended with 1.67 g of KNO_3 (96.5% ^{15}N atom abundance) dissolved in 1000 mL of deionized water. The addition of KNO_3 was equivalent 2.5 kg N/ha. After mixing the KNO_3 solution into the soil as thoroughly as possible, the soil was returned to the frames. The two remaining plots in each block were screened, mixed, and returned as above but did not receive the KNO_3 labelled with ^{15}N.

For sampling purposes one labelled and one unlabelled plot in each block was designated for winter sampling, while the remaining labelled and unlabelled plots were reserved for sampling in the spring. The purpose of this procedure was to eliminate the effects of coring holes on moisture redistribution during the winter-spring transition. Winter plots were initially sampled on November 15, 1980, just as the soil was freezing. Subsequent winter samplings were carried out on January 2 and March 5, 1981. The spring frames were sampled only once on May 9, 1981 at Breton; May 6 under stubble at Ellerslie and May 30 under fallow.

Four cores were removed from designated plots at each sampling date. The cores were divided into sections and then mixed by depth section (0-13, 13-30, and 30-60 cm) to form composite samples. Treatment of samples with respect to determination of moisture content, drying and grinding was identical to samples obtained in Experiment 1980A. An additional step in pre-analytical treatment was required to prepare the soils for total-N analysis: 50 g of the coarse ground (2 mm) soil was further reduced in size using a swing mill and screened to pass 0.15 mm sieve openings.

Experiment 1981A

Microplots were established in late October 1981 on barley stubble in the Breton and Malmo soils. Plastic cylinders 10 by 20 cm (inside diameter x length) were driven into the ground to at depth of 18 cm. The soil within the cylinders was removed to a depth of 15 cm and discarded. Caps were placed over the empty cylinders, and wire stakes marked with tape placed by each cylinder to facilitate locating them under snow cover.

In mid-November, soil from adjacent plots which had been labelled with ^{15}N as NO_3^- in October of 1980 and cropped to barley over the summer of 1981 was removed from the field. This soil was passed through a screen with 1 cm openings and stored moist at 2°C. On November 23 it was added to the cylinders prepared earlier. Bulk densities approximating those of surrounding soil were achieved by packing 1250 g (1.06 g/cm^3) of the Breton soil and 1130 g (0.96 g/cm^3) of the Malmo soil into a 15 cm length of each cylinder.

Sixteen microplots were prepared in a complete block design with four replicates and four sampling times as treatments. Microplots were initially sampled on December 2, 1981 and subsequently on January 3, March 23 and May 3, 1982. Sampling procedure at each sampling date consisted of removing one cylinder in its entirety from each replicate. The soil inside the cylinders was extruded into plastic bags which were then sealed to prevent moisture loss. After thawing, the samples were mixed and 30 g removed for determination of moisture content. The remaining sample was spread thinly to dry at room temperature. Dried samples were ground to pass through 2 mm sieve openings and a representitive 200 g subsample collected for analyses in the laboratory.

Additional samples from the 15-30 and 30-45 cm depths were removed from below the final cylinders harvested in May. These samples were dried and ground as outlined earlier. They were later analyzed to determine if ^{15}N had moved down the soil profile over the winter.

Experiment 1981B

This experiment was conducted concurrently with Experiment 1981A. Microplots were established as outlined earlier on Breton and Malmo soil. Soil from barley stubble plots, adjacent to the microplots at each site, was screened, mixed, and weighed into 1250 g portions of the Breton soil and 1130 g portions of the Malmo soil. Each portion was amended with 6.28 mg of N as KNO_3 (96.5% ^{15}N atom abundance). Half the plots at each sites were further amended with 2.36 g of coarsely ground barley plants (grain and straw). The amended soils were placed in the cylinders on November 23, 1981. The procedure for collecting and handling samples was identical to Experiment 1981B.

C. LABORATORY ANALYSIS

Mineral-N

Experiment 1980A

Mineral-N was extracted from the soil using a modification of the method outlined by McKeague (1978). Twenty grams of soil and 100 mL of 2N KCl were shaken together for one hour. The extract was filtered through Whatman No. 40 paper and aliquots of the filtrate analyzed by Technicon auto-analyzer II for NH_4^+-N and NO_3^--N (Industrial Methods No. 98-70W and 100-70W-B for NH_4^+-N and NO_3^--N respectively).

Experiment 1980B

Extraction of mineral-N followed the procedure outlined above except 40 g of soil and 100 mL of 2N KCl were used. The concentration of NH_4^+-N and NO_3^--N in 50 mL aliquots of the extract were determined by two step steam distillation with MgO and Davarda's alloy (Bremner, 1965a). Distillate was collected in 5 mL of 2% boric acid solution and titrated with 0.01 N H_2SO_4.

Following titration the distillate was prepared for N isotope analysis by further acidfying with 0.3 mL of 1 N H_2SO_4, and spiking when necessary with $(NH_4)_2SO_4$, 0.3658% ^{15}N atom abundance (APPENDIX B-Table 1). Sufficient $(NH_4)_2SO_4$ was added to accomplish the following objectives:

1. Dilute the N in the distillate to below 2% ^{15}N atom abundance.
2. Raise the N content of the distillate to between 1000 and 1500 μg.

When more than 1500 μg of N as $(NH_4)_2SO_4$ was required to reduce the enrichment below 2%, the distillate was split into portions each containing approximately 800 to 1200 μg of N. Following acidification and spiking, $(NH_4)_2SO_4$ crystals were prepared by evaporating the distillate to dryness on a sandbath at 60°C.

Experiment 1981A and 1981B

Soil samples (75 g) were placed in 500 mL Erlenmeyer flasks with 150 mL of 2 N KCl and shaken for 1 hour. The resulting slurry was transferred quantitatively to a Buchner funnel and leached under vacuum with five 20 mL aliquotes of KCl. The volume of filtrate was adjusted to a final volume of 250 mL by adding additional KCl. Determination of NH_4^+-N and NO_3^--N was performed on 150 mL aliquots of the extract as outlined for Experiment 1980B. Ammonium sulfate crystals, for analysis by mass spectrometer, were prepared from the resulting distillates as in Experiment 1980B.

The soil remaining in the Buchner funnel was flushed with 50 mL of deionized water to remove residual KCl, transferred to a weighing can and dried in an oven at 40°C. The dried soil was ground to pass 0.15 mm in a swing mill, and was used in determination of organic-N by Kjeldahl digestion.

Kjeldahl analysis for total or organic-N

Experiment 1980B

Total-N was determined using the methods of Bremner (1965b) with pretreatment to include NO_2^--N and NO_3^--N. Soils were first treated with $KMnO_4$ and H_2SO_4 to oxidize NO_2^- to NO_3^- and then with reduced Fe to reduce NO_3^- to NH_4^+. Following pretreatment samples were digested for 1 1/2 hours at 220°C and 2 hours at 360°C on a Technicon 20 Block Digester. Nitrogen content of the digest was determined following the steam distillation method of Bremner (1965b). Preparation of $(NH_4)_2SO_4$ crystals for ^{15}N analysis followed the procedure outlined under mineral-N.

Experiments 1981A and 1981B

Analysis for organic-N (mineral-N had been removed by leaching with KCl) followed the methods for Kjeldahl digestion outlined by Bremner (1965b), except that the pretreatment for inclusion of NO_2^--N and NO_3^--N was deleted from the procedure. The digests were analyzed for N content by steam distillation (Bremner, 1965b) and distillates titrated and prepared for ^{15}N analysis as outlined under mineral-N.

^{15}N Analysis

Ammonium sulfate crystals were oxidized under vacuum to $N_2(g)$ by LiOBr following the Sprinson and Rittenberg (1948) procedure as modified by Bremner (1965c). The ratio of ^{15}N to ^{14}N atoms in the N_2 was determined on a Micromass 602, 60° sector-type mass spectrometer. The atom abundance of ^{15}N was calculated from the isotope ratios employing the equations of Hauck (1982). Using percent ^{15}N atom excess values, percent recovery of added nitrogen was determined in the various soil N fractions of each sample.

Analysis for ^{15}N was performed on the surface samples for all sampling dates. Further ^{15}N analysis of selected samples from the 13-30, 30-60 cm depths (Experiment 1980B) or 15-30, 30-45 cm depths (Experiments 1981A and 1981B) was performed to determine if ^{15}N had moved down the profile. Background ^{15}N atom abundance in the Breton and Malmo soils was determined by analyzing total and mineral-N samples obtained from the unlabelled plots of Experiment 1980B (APPENDIX B-Tables 2 and 3).

D. STATISTICAL ANALYSIS

Experiment 1980A

Each set of stubble or fallow plots in Experiment 1980A was treated as a completely randomized experiment with sampling time as treatment. Analysis of variance on NH_4^+-N,

NO_3^--N and mineral-N was performed on data from the 0-15, 15-30, and 30-60 cm depths as well as the summarized data for the profile, 0-60 cm. Additional analyses of variance in a simple 4x2 factorial design was performed on the pooled data for those soils where plots had been established on stubble and fallow. This procedure was used to test for differences between stubble and fallow over time. Difference between means were statistically verified using the method of least significant difference (LSD) at the 5% level of probability as outlined by Steel and Torrie (1980).

Experiment 1980B

Analysis of variance was performed for a randomized complete block design in three replicates with sampling times as treatments as outlined by Steel and Torrie (1980). ANOVAs were generated for data arising from the NH_4^+-N, NO_3^--N, organic-N, and total-N fractions as well as ^{15}N atom abundance for each of the above. Differences between means were verified using LSD ($p=0.05$).

Experiment 1981A

Analysis of variance was performed as a randomized complete block in four replicates with sampling times as treatment. Differences between the means at each sampling time for the NH_4^+-N, NO_3^--N, organic-N, and total-N data sets and the ^{15}N atom abundance of each fraction were checked for statistical significance using LSD ($p=0.05$).

Experiment 1981B

Experiment 1981B was set out as a 2x4 factorial in four replicates. The two treatments at the first level were residues added or not added and the four treatments at the second level the four sampling dates. Means arising from the NH_4^+-N, NO_3^--N, organic-N, and total-N data and the mean ^{15}N atom abundance of each fraction were distinguished by LSD ($p=0.05$).

IV. RESULTS AND DISCUSSION

A. EXPERIMENT 1980A: CHANGES IN MINERAL-N BETWEEN NOVEMBER AND MAY

Results: Experiment 1980A

Comparison of NH_4^+, NO_3^-, and mineral-N levels within each soil over time showed that the size of the pools changed between late fall and spring (Tables 2 to 8). No consistent pattern of accumulation or loss was discernible during the period between the late fall sampling in November and the late winter sampling in March. The quantity of NH_4^+, NO_3^-, or mineral-N increased in some soils at some depths, declined in others and in some did not change. The level of mineral-N rose during the late winter to spring period in six out of seven soils. The exception was the Navarre stubble soil in which no significant change was evident.

The net change in mineral-N between fall and spring in the surface 60 cm ranged from -4.1 kg N/ha to 85.3 kg N/ha. The average net increase in mineral-N was 53 kg N/ha (Table 9). Increases in NH_4^+ levels accounted for 30 kg N/ha of the accumulated mineral-N while the remaining 23 kg N/ha accumulated as NO_3^-. Accumulations were largest in the surface horizons, averaging 22 kg N/ha of mineral-N. Smaller increases of 13 kg N/ha and 18 kg N/ha of mineral-N were observed in the 15-30 and 30-60 cm depths respectively. Fallow soils tended to accumulate more mineral-N over the winter than stubble soils. The average increase between fall and spring was 62 kg N/ha under fallow compared to 39 kg N/ha under stubble. In the Didsbury, Malmo, and Navarre soils statistical comparisons between stubble and fallow over time confirmed that the accumulation of mineral-N proceeded to a greater extent between November and May in fallow soils.

Table 2. Overwinter changes in the NH_4^+-N, NO_3^--N, and mineral-N levels of a fallow Breton soil.

Nitrogen form	Depth (cm)	Date Sampled[1] Nov 16/80	Dec 12/80	Mar 4/81	May 2/81
NH_4^+-N (kg N/ha)	0-15	7.0 b	7.3 b	6.6 b	16.1 a
	15-30	9.7 b	8.6 b	8.6 b	15.9 a
	30-60	16.4 c	22.0 b	22.0 b	36.0 a
	0-60	33.1 b	37.9 b	36.2 b	68.0 a
NO_3^--N (kg N/ha)	0-15	9.9 b	5.4 c	4.5 c	28.4 a
	15-30	4.9 b	7.1 ab	9.7 a	8.4 ab
	30-60	4.7 b	6.1 ab	6.1 ab	7.5 a
	0-60	19.5 b	18.6 b	20.3 b	44.3 a
Mineral-N (kg N/ha)	0-15	16.7 b	12.5 c	11.1 c	44.5 a
	15-30	14.6 b	15.7 b	18.5 b	24.0 a
	30-60	21.5 c	28.1 b	28.1 b	43.5 a
	0-60	52.8 b	56.3 b	57.7 b	112.0 a

[1] Means within each row followed by different letters are significantly different by LSD ($p=0.05$).

Table 3. Overwinter changes in the NH$_4^+$-N, NO$_3^-$-N, and mineral-N levels of a fallow Didsbury soil.

Nitrogen form	Depth (cm)	Date Sampled[1]			
		Nov 12/80	Jan 2/81	Mar 6/81	May 3/81
NH$_4^+$-N (kg N/ha)	0-15	10.5 b	10.5 b	7.7 b	32.3 a
	15-30	8.8 b	9.0 b	8.4 b	19.7 a
	30-60	15.7 b	15.7 b	14.3 b	39.4 a
	0-60	35.0 b	35.2 b	30.4 b	91.4 a
NO$_3^-$-N (kg N/ha)	0-15	59.4 b	70.3 a	73.0 a	60.2 b
	15-30	52.7 a	61.7 a	60.9 a	57.7 a
	30-60	96.4 a	107.3 a	111.2 a	70.8 a
	0-60	208.5 b	239.3 a	245.1 a	188.7 b
Mineral-N (kg N/ha)	0-15	69.9 c	80.8 b	80.7 b	92.5 a
	15-30	61.5 b	70.7 ab	69.3 ab	77.4 a
	30-60	112.1 a	123.0 a	125.5 a	110.2 a
	0-60	243.5 b	274.5 a	275.5 a	280.1 a

[1] Means within each row followed by a different letter are significantly different by LSD ($p=0.05$).

Table 4. Overwinter changes in the NH_4^+-N, NO_3^--N and mineral-N levels of a stubble Didsbury soil.

Nitrogen analysis	Depth (cm)	Date Sampled[1]			
		Nov 12/80	Jan 2/81	Mar 6/81	May 3/81
NH_4^+-N (kg N/ha)	0-15	12.9 b	12.7 b	9.4 b	39.3 a
	15-30	9.6 b	7.3 b	5.9 b	39.3 a
	30-60	12.6 b	11.7 b	9.2 c	35.0 a
	0-60	35.1 b	31.7 bc	24.5 c	96.5 a
NO_3^--N (kg N/ha)	0-15	15.8 b	9.7 b	15.8 b	25.5 a
	15-30	6.3 b	7.5 b	2.9 b	18.0 a
	30-60	5.8 ab	4.4 ab	0.5 b	8.3 a
	0-60	27.9 b	21.6 b	19.2 b	51.8 a
Mineral-N (kg N/ha)	0-15	28.7 b	22.4 b	25.2 b	64.8 a
	15-30	15.9 b	15.1 b	8.8 b	40.2 a
	30-60	18.4 b	16.1 bc	9.7 c	43.3 a
	0-60	63.0 b	53.3 bc	43.7 c	148.3 a

[1] Means within each row followed by a different letter are significantly different by LSD ($p=0.05$).

Table 5. Overwinter changes in the NH_4^+-N, NO_3^--N, and mineral-N levels of a fallow Malmo soil.

Nitrogen form	Depth (cm)	Date Sampled[1]			
		Nov 19/80	Dec 29/80	Mar 3/81	May 26/81
NH_4^+-N (kg N/ha)	0-15	14.0 a	12.4 a	14.2 a	11.9 a
	15-30	10.3 b	10.1 b	11.3 b	18.7 a
	30-60	16.3 b	15.3 b	16.7 b	26.0 a
	0-60	40.6 a	37.8 a	44.2 a	56.6 a
NO_3^--N (kg N/ha)	0-15	21.6 b	28.7 b	23.6 b	62.4 a
	15-30	5.4 b	13.1 a	8.5 ab	14.4 a
	30-60	2.8 c	8.8 b	4.2 c	16.3 a
	0-60	29.8 c	50.6 b	36.3 c	93.1 a
Mineral-N (kg N/ha)	0-15	35.6 b	41.2 b	37.8 b	74.3 a
	15-30	15.7 c	23.2 b	19.8 bc	33.1 a
	30-60	19.1 c	24.1 b	20.9 bc	42.3 a
	0-60	70.4 b	88.4 b	80.5 b	149.7 a

[1] Means within each row followed by a different letter are significantly different by LSD ($p=0.05$).

Table 6. Overwinter changes in the NH_4^+-N, NO_3^--N, and mineral-N levels of a stubble Malmo soil.

Nitrogen form	Depth (cm)	Date Sampled[1]			
		Nov 19/80	Dec 29/80	Mar 3/81	May 4/81
NH_4^+-N (kg N/ha)	0-15	11.8 a	17.6 a	11.2 a	17.2 a
	15-30	9.1 b	10.7 ab	10.7 ab	12.4 a
	30-60	15.5 b	14.7 b	16.0 b	33.3 a
	0-60	36.4 b	43.0 ab	37.9 b	62.9 a
NO_3^--N (kg N/ha)	0-15	25.9 a	14.3 ab	10.9 b	24.8 a
	15-30	10.2 b	22.1 a	18.7 a	10.8 b
	30-60	4.0 b	13.3 a	12.0 a	16.4 a
	0-60	40.1 a	49.7 a	41.6 a	52.0 a
Mineral-N (kg N/ha)	0-15	37.7 ab	31.9 ab	22.1 b	42.0 a
	15-30	19.3 b	32.8 a	29.4 a	23.2 b
	30-60	19.5 b	28.0 b	28.0 b	49.7 a
	0-60	76.5 b	92.7 ab	79.5 b	114.9 a

[1] Means within each row followed by a different letter are significantly different by LSD ($p=0.05$).

Table 7. Overwinter changes in the NH_4^+-N, NO_3^--N, and mineral-N levels of a fallow Navarre soil.

Nitrogen form	Depth (cm)	Date Sampled[1]			
		Nov 17/80	Dec 31/80	Mar 4/81	May 3/81
NH_4^+-N (kg N/ha)	0-15	12.4 ab	18.8 a	14.7 ab	9.4 b
	15-30	13.2 c	13.6 c	15.7 b	20.3 a
	30-60	17.3 b	17.8 b	22.9 b	33.7 a
	0-60	42.9 c	50.2 b	53.3 b	63.4 a
NO_3^--N (kg N/ha)	0-15	13.0 b	10.0 b	7.3 b	39.7 a
	15-30	9.9 c	20.8 a	14.3 b	23.1 a
	30-60	10.3 b	13.6 b	13.6 b	23.9 a
	0-60	33.2 b	44.4 b	35.2 b	86.7 a
Mineral-N (kg N/ha)	0-15	25.4 b	28.8 b	22.0 b	49.1 a
	15-30	23.1 d	34.4 b	29.0 c	43.4 a
	30-60	27.6 b	31.4 b	36.5 b	57.6 a
	0-60	76.1 b	94.6 b	88.5 b	150.1 a

[1] Means within each row followed by a different letter are significantly different by LSD ($p=0.05$).

Table 8. Overwinter changes in the NH_4^+-N, NO_3^--N, and mineral-N levels of a stubble Navarre soil.

Nitrogen form	Depth (cm)	Date Sampled[1]			
		Nov 17/80	Dec 31/80	Mar 4/81	May 3/81
NH_4^+-N (kg N/ha)	0-15	8.5 a	12.3 a	11.5 a	6.5 a
	15-30	8.0 b	8.0 b	12.1 a	8.0 b
	30-60	12.6 b	11.2 b	16.4 a	10.3 b
	0-60	29.1 b	31.5 ab	40.0 a	24.9 b
NO_3^--N (kg N/ha)	0-15	4.1 a	3.8 a	0.9 b	6.5 a
	15-30	1.8 bc	4.6 a	3.6 ab	1.6 c
	30-60	1.4 a	2.3 a	0.9 a	1.9 a
	0-60	7.3 ab	10.7 a	5.4 b	7.4 ab
Mineral-N (kg N/ha)	0-15	12.6 a	16.1 a	12.4 a	10.4 a
	15-30	9.8 b	12.6 ab	15.7 a	9.6 b
	30-60	14.0 a	13.5 a	17.3 a	12.2 a
	0-60	36.4 ab	42.2 a	42.2 a	32.3 b

[1] Means within each row followed by a different letter are significantly different by LSD ($p=0.05$).

Table 9. Changes in NH_4^+-N, NO_3^--N, and mineral-N levels between November and May in four fallow and three stubble soils (0-60 cm).

Tillage	Nitrogen form	Nitrogen content[1] (kg N/ha) November	January	March	May	Change in N content November to May
Fallow	NH_4^+-N	38	40(2)	42(3)	70(29)	32
	NO_3^--N	73	88(15)	84(-4)	103(19)	30
	Mineral-N	111	128(17)	125(-3)	173(48)	62
Stubble	NH_4^+-N	34	35(1)	34(-1)	61(27)	27
	NO_3^--N	25	27(2)	22(-5)	37(15)	12
	Mineral-N	59	59(0)	56(-3)	98(42)	39
Combined	NH_4^+-N	36	38(2)	38(0)	66(28)	30
	NO_3^--N	52	62(10)	57(-5)	75(18)	23
	Mineral-N	88	100(12)	95(-5)	141(46)	53

[1] Values in brackets represent change in N (kg N/ha) from previous sampling time. Sums may not be exact due to rounding.

Discussion: Experiment 1980A

The results of Experiment 1980A are in general agreement with similar studies conducted on the Canadian prairies. Campbell and Biederbeck (1981) and Campbell *et al.* (1970b) reported changes in the NO_3^- levels of southern Saskatchewan soils while the soils were frozen. Malhi and Nyborg (1985) in a study of ten central Alberta soils found a trend of mineral-N build up during the winter followed by losses during the spring thaw. In the present study accumulation of mineral-N were evident between November and March in the Didsbury fallow soil (Table 3), which also showed a decline in NO_3^- levels between March and May. No general trend of increase and subsequent decline is evident when the results of all seven soils are viewed collectively. The rapid increase of mineral-N between late winter and spring sampling dates is not similiar to the trends observed by Malhi and Nyborg (1985). However, the soils in the spring had been warm and relatively dry (i.e. below saturation) for a period of several weeks prior to sampling. As a result, the observed accumulation of mineral-N may have arisen during a period of rapid post thaw mineralization that masked losses during the spring thaw. The effect of thawing frozen soil on mineral-N levels has been previously documented by Mack (1963) and Hinman (1970). Both authors reported that thawing promotes mineralization and accumulation of mineral-N.

Based on the changes in mineral-N reported in the present study, fallow soils appear to be more active than stubble soils between fall and spring. Similar results were reported by Malhi and Nyborg (1985), who observed that net overwinter gains in mineral-N and losses in the spring were greater in fallow than in stubble soils. Results of this nature may be be misleading in that they measure the net change in the pool rather than the activity of the processes mediating gain and loss. Fallowing can lead to greater mineralization of N for a number of reasons: better aeration of the soil (Campbell, 1978), higher microbial activity due to better moisture conditions (Shields *et al.*, 1973), entry of previously occluded low C:N substrates into the available pool by tillage disruption of aggregates (Paul and van Veen, 1979). Net accumulation of N entering the mineral-N pool can also be enhanced in fallow soils by low rates of removal. McGill *et al.* (1981) found that immobilization was lower in fallow compared to cropped soils due to the absence of root exudates and sloughing of dead roots. Removal of mineral-N through denitrification can also be reduced by lack of available C in the absence of crop residues and exudates (Terry and Tate, 1980). Accumulation of mineral-N as observed in experiment 1980A may or may not imply greater activity of the processes augmenting the mineral-N pool when fallow-stubble comparisons are made. It does indicate that the balance between the two types of processes changes as soils go from stubble to fallow. The results of the present study suggest that the direction in which the balance shifts, towards net accumulation in fallow soils, is maintained over the winter.

The preceding discussion points out one of the limitations of using net changes in mineral-N as an indicator of activity in the nitrogen cycle. An observation of change in the level of mineral-N indicates that one or more of the processes involved in additions to or removals from the pool are active. The opposite observation, no change in mineral-N over time, is not a reliable indicator of lack of activity but merely that the opposing processes of gain and loss are in equilibrium. With respect to the soils used in this experiment which exhibited no overwinter change in mineral-N, the nature of this equilibrium cannot be determined. It may be dynamic in that balanced turnover of the pool is taking place or, due to the restrictions of temperature or other environmental variables, it may be static with little or no N flowing through the inorganic pool.

The source of nitrogen entering the mineral-N pool cannot be directly identified using the results of Experiment 1980A. Several processes are possible contributors to the rise in mineral-N levels. Gains in NH_4^+ as well as NO_3^- were observed in most of the plots. This implies that biological mineralization or release of fixed NH_4^+ was taking place. Nitrate levels also rose in the late winter to spring period. There is no way of determining directly whether this rise was due to movement of NO_3^- up the profile as the surface dried or arose from nitrification of NH_4^+.

There is little evidence of the movement of NO_3^- towards the surface as the soils started to freeze in the fall such as reported by Campbell *et al.* (1970b). Kryzanowski *et al.* (1984)

used the results presented here in combination with the results of similar experiments to determine the best time and sampling depth for correlating mineral-N levels to crop yield. In their examination of the data, they found little evidence of vertical NO_3^- movement over the winter. The Didsbury fallow soil may be an exception in that NO_3^- levels rose during the fall-winter transition. Furthermore, high levels of NO_3^- were present at lower depths of the profile, a condition prerequisite for freeze-induced upward migration of NO_3^- (Miller, 1980). Other soils used in the present study had relatively low levels of NO_3^- below 15 cm and the contribution of freeze induced migration to overwinter accumulation of NO_3^- in the top 15 cm of their profiles appears negligible.

Several lines of indirect evidence imply that at least a portion of the N entering the pool as NH_4^+ arose from mineralization. Gains in NH_4^+ were greater in fallow than stubble, a trend commonly repotred in studies of mineralization during the growing season. Increases in NH_4^+ concentration were greatest in the 0-15 cm depth and least in the 30-60 cm depth, and thus followed the gradient of declining microbial activity with depth (Alexander, 1977; Cho *et al*, 1979). Finally, increases in NH_4^+ were most evident following a period of the year, the winter-spring transition, when freeze-thaw cycles are common. Mack (1963) and Hinman (1970) reported that freeze-thaw cycles promote mineralization in the laboratory, a phenomenon which, based on the data from the present study, appears to take place in field soils as well.

As was pointed out earlier, the trend of spring losses reported by Malhi and Nyborg (1985) was not evident in the soils used in the present study. Net negative changes in various depths and mineral-N fractions were evident in several of the soils over the winter. For example, Didsbury fallow soil showed a decline in NO_3^- between March 6 and May 3, 1981 (Table 3). Mineral-N levels also dropped in the Didsbury stubble soil between November 12, 1980 and March 6, 1981 (Table 4).

Summary: Experiment 1980A

Overwinter losses cannot be assigned, based on the changes in mineral-N observed in this experiment, to immobilization, denitrification, or leaching with any certainty. Nor can loss mechanisms be eliminated on the basis of restrictive soil temperature or moisture conditions since insufficient data on these variables was collected. Gains in mineral-N over the winter cannot be partitioned between discrete mechanisms for similar reasons. Small net changes in mineral-N were observed in some soils while they were frozen. Net changes in mineral-N content of the seven soils examined in this study were greatest between March and May. Of the 53 kg N/ha of mineral-N that accumulated on average over the winter, 46 kg N/ha or 87% arose during this latter period.

B. EXPERIMENT 1980B: LOSSES OF MINERAL-N BETWEEN NOVEMBER AND MAY

Results: Experiment 1980B

Background ^{15}N atom abundance

Samples obtained from the nil plots were analyzed to determine the background ^{15}N atom abundance of the NH_4^+,NO_3^-, and total-N fractions. Variability in background ^{15}N atom abundance in the Breton and Malmo soils was relatively large and is due in part to the natural spatial variability of the soil and in part to experimental error (Table 10).

Net changes in mineral-N between November and May

Net changes in the mineral-N pool can be calculated from the data presented in Tables 11 and 13. There was a small net increase in mineral-N, average 4.4 μg N/g, between November and March at all sites. Mineral-N levels rose an average of 50.1 μg N/g at Breton between early

Table 10. Summary of natural abundance values invarious N fractions of a Breton and Malmo soil.

Soil series	Form of N	Atomic Abundance[1] (%)	Coefficient of variation (%)
Breton	NH_4-N	0.3682 ± 0.0177	2.1
	NO_3-N	0.3690 ± 0.0202	1.7
	Total-N	0.3676 ± 0.0012	0.1
Malmo	NH_4-N	0.3672 ± 0.0085	1.0
	NO_3-N	0.3678 ± 0.0112	0.5
	Total-N	0.3672 ± 0.0015	0.2

[1] Means reported ± 95% confidence limits.

Table 11. Overwinter changes in the NH_4^+, NO_3^-, and mineral-N content of a Breton soil 1980-81 (0-13 cm).

Treatment	N form	Amount of N present at different sampling dates[1] (μg N/g)			
		November	January	March	May
Fallow	NH_4^+	3.7 a	3.1 a	5.2 b	8.1 c
	NO_3^-	9.2 a	3.6 a	11.1 a	55.8 b
	Mineral-N	12.9 a	6.7 a	16.4 a	63.9 b
Stubble	NH_4^+	4.0 a	3.2 a	5.3 b	6.7 c
	NO_3^-	3.7 a	2.3 a	7.7 b	59.0 c
	Mineral-N	7.7 a	5.5 a	13.0 b	65.7 c

[1] Values in rows followed by different letters are asignificantly different by LSD ($p=0.05$).

Table 12. Recovery of ^{15}N enriched fertilizer applied in October 1980 as NO_3^- to a Breton soil 1980-81 (0-13 cm).

Treatment	Form of N		Fertilizer N recovery at different sampling dates[1] [2]			
			November	January	March	May
Fallow	NH_4^+	(μg N/g)	2×10^{-3} a	4×10^{-3} a	2×10^{-3} a	5×10^{-3} a
		(%)	0.1	0.2	0.1	0.2
	NO_3^-	(μg N/g)	1.34 a	0.16 b	0.31 b	0.43 b
		(%)	58.6	7.1	20.9	18.6
	Organic-N[3]	(μg N/g)	0.32 a	0.15 a	0.04 a	0.31 a
		(%)	13.9	6.4	1.7	13.5
	Total-N	(μg N/g)	1.66 a	0.31 b	0.35 b	0.74 b
		(%)	72.6	13.7	15.2	32.3
Stubble	NH_4^+	(μg N/g)	3×10^{-3} a	6×10^{-3} ab	9×10^{-3} b	0×10^{-3} c
		(%)	0.2	0.3	0.4	0.0
	NO_3^-	(μg N/g)	0.64 a	0.10 b	0.08 b	0.22 b
		(%)	27.6	4.3	3.4	9.5
	Organic-N[3]	(μg N/g)	0.49 a	0.18 b	0.25 b	0.10 b
		(%)	20.9	7.9	10.4	3.9
	Total-N	(μg N/g)	1.13 a	0.29 b	0.34 b	0.32 b
		(%)	48.7	12.5	14.2	13.4

[1] Fertilizer N added at a rate of 2.28 μg N/g soil and 2.32μg N/g soil to the fallow and stubble plots respectively.
[2] Values in rows followed by different letters are significantly different by LSD ($p=0.05$).
[3] Recovery of ^{15}N in organic-N fraction was determined by difference between total-N and NH_4^+-N plus NO_3^--N.

Table 13. Overwinter changes in the NH_4^+, NO_3^-, and mineral-N content of a Malmo soil 1980-81 (0-13 cm).

Treatment	N Form	Amount of N present at different sampling dates[1] (μg N/g) November	January	March	May
Fallow	NH_4^+	6.2 a	6.6 a	5.7 a	5.7 a
	NO_3^-	6.2 a	12.2 b	13.5 b	25.8 c
	Mineral-N	12.4 a	18.8 b	19.2 b	31.5 c
Stubble	NH_4^+	6.8 ac	5.8 b	6.2 bc	7.5 a
	NO_3^-	9.8 ab	12.0 a	12.4 a	3.9 b
	Mineral-N	16.6 a	17.8 a	18.6 a	11.4 b

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[1] Values in rows followed by different letters are significantly different by LSD ($p=0.05$).

Table 14. Recovery of ^{15}N enriched fertilizer applied in October 1980 as NO_3^- to a Malmo soil 1980-81 (0-13 cm).

Treatment	Form of N		Fertilizer ^{15}N recovery at different sampling dates[1] [2]			
			November	January	March	May
Fallow	NH_4^+	(μg N/g)	$8x10^{-3}$ a	$4x10^{-3}$ b	$5x10^{-3}$ b	$3x10^{-3}$ b
		(%)	0.3	0.2	0.2	0.1
	NO_3^-	(μg N/g)	0.96 a	0.62 ab	0.8 a	0.59 b
		(%)	39.6	25.5	44.5	24.5
	Organic-N[3]	(μg N/g)	0.55 a	0.64 a	0.60 a	0.48 a
		(%)	22.8	26.6	24.9	19.9
	Total-N	(μg N/g)	1.52 a	1.26 ab	1.69 a	1.07 b
		(%)	63.1	52.3	70.1	42.7
Stubble	NH_4^+	(μg N/g)	$5x10^{-3}$ a	$5x10^{-3}$ a	$5x10^{-3}$ a	$10x10^{-3}$ b
		(%)	0.2	0.2	0.2	0.4
	NO_3^-	(μg N/g)	1.21 a	0.60 ab	0.49 b	0.03 b
		(%)	44.0	21.6	17.8	1.3
	Organic-N[3]	(μg N/g)	0.68 a	0.62 a	0.68 a	0.83 a
		(%)	24.6	22.4	24.6	30.1
	Total-N	(μg N/g)	1.89 a	1.2[illegible]b	1.18 ab	0.87 b
		(%)	68.4	44.3	42.6	31.5

[1] Fertilizer N added at a rate of 2.41 μg N/g soil and 2.7 6 μg N/g soil to the fallow and stubble plots respectively.
[2] Values in rows followed by different letters are significantly different by LSD ($p=0.05$).
[3] Recovery of ^{15}N in organic-N fraction was determined by difference between total-N and NH_4^+-N plus NO_3^--N.

Table 15. Percent recovery in May 1981 of ^{15}N enriched NO_3^- applied to a Breton and Malmo soil in October 1980.

Recovery in (%)	Depth (cm)	Breton fallow	Breton stubble	Malmo fallow	Malmo stubble
NH_4^+	(0-13)	0.2	0.0	0.1	0.4
NO_3^-	(0-13)	18.6	9.5	24.5	1.1
Organic-N[1]	(0-13)	13.5	3.9	19.9	30.1
Total-N	(13-30)	32.3	13.4	42.7	31.5
Total-N	(13-30)	0.4	0.1	0.4	0.1
Total-N	(30-60)	0.0	0.0	0.0	0.0
Total-N	(0-60)	32.7	13.5	44.9	31.7
Transferred out of NO_3^- pool(%)	(0-13)	81.4	90.5	75.5	98.9
Transferred out of soil system (%)	(0-60)	67.3	86.5	55.1	68.3

[1] Values for organic-N determined by difference between total-N (0-13 cm) and NH_4^+-N plus NO_3^--N.

March and mid-May. As the soils had been warm and well drained for a period of three weeks prior to sampling this increase is probably due to past thaw rather than winter mineralization. Similar observations were made in the Malmo soil. Stubble plots sampled in early May, within a few days of the transition from anaerobic to aerobic conditions, showed a net loss of 7.2 μg N/g over the March sampling. The fallow plots, sampled in late May, show an increase over the March sampling of 12.3 μg N/g.

Recovery of fall applied ^{15}N

Recovery of ^{15}N as NO_3^- was significantly lower in the spring sampling compared to the fall sampling, indicating that a transfer of N out of the mineral-N pool took place between November and May (Tables 12 and 14). In May the ^{15}N as NO_3^- remaining in the 0-13 cm depth accounted for 1.1 to 24.5% of the ^{15}N enriched fertilizer added in October. The N transferred out of the NO_3^- pool was in part immobilized, 3.9 to 30.1%, and in very small part moved down the profile, less than 0.5% in all plots. The difference between total losses and losses accounted for by immobilization and leaching ranged from 34.5% to 78.4% of added N and has been attributed to denitrification (Table 15).

Amounts of ^{15}N immobilized in the organic-N pool varied considerably between November and May but the differences are only statistically verifiable in the Breton stubble plots (Table 12). A considerable amount of ^{15}N was immobilized in the late fall between the time of application in October and the initial sampling date in mid-November (Tables 12 and 14).

Analysis of selected samples obtained from the 13-30 cm and 30-60 cm depths in December and March showed that there was no movement of NO_3^- down the profile during the late fall or winter of 1980-81 (Table 16). Similarily, the ^{15}N atom abundance levels of samples from the 30-60 cm depth in May were indistinguishable from the natural abundance determinations for these depths.

Table 16. Percent atomic abundance of total-N fraction in matched tagged and nil plots at various depths and times.

	Depth (cm)	Sampling date	^{15}N atom abundance (%)	
			Tagged plots	nil plots
Breton fallow	15-30	January	0.3674	0.3676
		March	0.3677	0.3676
		May	0.3703	0.3674
	30-60	May	0.3670	0.3672
Breton stubble	15-30	January	0.3676	0.3675
		March	0.3676	0.367[illegible]
		May	0.3683	0.36[illegible]
	30-60	May	0.3669	0.3672
Malmo fallow	15-30	January	0.3668	0.3674
		March	0.3671	0.3671
		May	0.3698	0.3671
	30-60	May	0.3683	0.3673
Malmo stubble	15-30	January	0.3671	0.3670
		March	0.3674	0.3673
		May	0.3682	0.3673
	30-60	May	0.3670	0.3673

Discussion: Experiment 1980B

Immobilization and mineralization

The priming effect of N fertilizers on mineralization/immobilization turnover, in which large additions of N enhance both processes, has been extensively documented (cf. Jansson and Persson, 1982; Campbell, 1978). In Experiment 1980B only small amounts of N were added, therefore, the immobilization observed in the late fall is probably not due to stimulation of the soil biota by the fertilizer. Several other anthropogenic factors may have stimulated late fall activity by the biomass. Campbell (1978) reported that tillage can stimulate immobilization by improving aeration and bringing standing stubble into contact with soil biota. Mixing the soil during preparation of the plots could thus be partly responsible for the rapid immobilization which occurred between addition of the ^{15}N in October and the initial sampling in mid-November. The amount of ^{15}N present in the organic form was higher in the stubble than in the fallow plots at the November sampling (Tables 12 and 14). This result suggests that residues did increase immobilization as outlined above. Aeration and mixing of residues may have enhanced immobilization above that which would have occurred if the plots were left undisturbed. This observation remains secondary to the observation that soil temperatures during October and November were not so low as to prevent immobilization in the Breton and Malmo soils.

The amount of mineral-N present at the time the ^{15}N was added in October was not determined in Experiment 1980B. Without a baseline, the net change of mineral-N in the late fall cannot be calculated. However, at the November sampling date ^{15}N arising from the fertilizer was already present in the NH_4^+ pool (Tables 12 and 14). While the amount of ^{15}N present as NH_4^+ is small, it does indicate that mineralization from the biomass was taking place concurrently with immobilization during the late fall.

The rise in the levels of mineral-N between March and May show a burst of mineralization occurred during this period. Similar sharp increases in the mineralization rate have been reported in overwinter field studies and in laboratory studies designed to simulate the winter-spring transition (Campbell and Biederbeck, 1972; Campbell *et al.*, 1970b; Campbell *et al.*, 1971; Hinman, 1970; Mack, 1963) and may be due to effects of the winter-spring transition on soil structure. Soulides and Allison (1961) found that freeze-thaw cycles break down soil aggregates. Soils in Alberta are normally subjected to several weeks of diurnal freeze-thaw cycles in the spring. If soil aggregates are disrupted by the action of ice formation and subsequent melting during this period then previously occluded organic matter of low C:N ratio may have been exposed to mineralization by the active biomass as suggested by Alexander (1977).

An alternate source of the mineral-N which rapidly accumulated during the immediate post thaw period is the biomass. Biederbeck and Campbell (1971) and Campbell *et al.* (1970a) showed in laboratory experiments that freeze-thaw cycles are extremely delitereous to the soil microflora. Campbell (1978) suggested that microbes killed by freeze-thaw cycles provide easily utilized substrate for surviving organisms and that the burst of mineralization observed in his earlier work (Campbell and Biederbeck, 1972; Campbell *et al.*, 1970b; Campbell *et al.*, 1971) was a by-product of biomass turnover. A study of microbial growth patterns by Monreal and McGill (1981), from which they concluded that populations of soil microorganisms obtain their metabolites mainly through scavenging the remains of their predecessors, supports the above hypothesis.

The results of the present study suggest that the Breton and Malmo soils behaved differently with respect to the source of mineral-N which accumulated between March and May. In the case of the Breton soil, the ^{15}N atom abundance of the NH_4^+ and organic-N pools in May are similiar (Table 17). Keeping in mind that ^{15}N immobilized over the winter would be largely concentrated in the biomass (i.e. the biomass N would be enriched to a greater degree than the organic N fraction as a whole), it is clear that NH_4^+ entering the pool was largely from sources other than the biomass. Results from the Breton soil in this instance support the first hypothesis that mineral-N is arising from previously occluded organic matter made available by freeze-thaw disruption of soil aggregates. The NH_4^+ pool in the Malmo soil on the other hand

Table 17. Percent ^{15}N atom abundance of various soil N fractions of the 0-13 cm depth in May 1981.

Soil	^{15}N atom abundance (%)[1]			
	Organic-N	NH_4^+-N	NO_3^--N	Total-N
Breton fallow	0.400 b	0.412 b	1.114 a	0.412 b
Breton stubble	0.373 c	0.369 c	0.726 a	0.385 b
Malmo fallow	0.375 c	0.424 b	2.555 a	0.386 c
Malmo stubble	0.381 c	0.493 b	1.043 a	0.382 c

[1] Values in rows followed by different letters are statistically different (LSD, p=0.01)

has a considerably greater enrichment than the organic-N fraction as a whole. This result suggests that the source of incoming NH_4^+ is in large part a highly tagged active fraction. In the Malmo fallow soil where mineral-N accumulated between March and late May, mineralization of dead biomass would appear to be the process responsible.

Leaching

The results of the present study, in which from 0.2 to 0.4% of the N applied as NO_3^- moved below the zone of application (Table 15), are in agreement with leaching trends observed in overwinter fertilizer studies conducted in central Alberta by Malhi and Nyborg (1983b). They found that ^{15}N applied in the fall as NO_3^- did had not moved below 60 cm by the spring of the following year. Both the Breton and Malmo soils have fine textured B horizons within their profiles (Howitt, 1981; Sanborn, 1981), and slow penetration of percolating waters through layers with low hydraulic conductivity may in part be responsible for the lack of downward NO_3^- movement. Field-Ridley (1975) noted that downward movement of NO_3^- proceeded relatively slowly in Manitoba clay and loam soils. In the Manitoba study leaching of applied NO_3^- below one metre was negligible over a two year fallow period.

Lack of moisture in the spring of 1981 is a second factor which may have restricted leaching losses in Experiment 1980B. Maximum recorded depth of snowcover was 120 mm and 180 mm over the Breton and Malmo plots respectively. Using the conversion factor for Alberta snowpacks estimated by Ferguson and Pollack (1971), the preceeding values would correspond to a liquid equivalent of 16 mm for Breton and 23 mm for Malmo. [1] Consequently there was little moisture available in the spring of 1981 to transfer NO_3^- down the profile.

Denitrification

Losses attributed to denitrification between November and May range from 34.5 to 78.4% of added ^{15}N (Table 15). Losses were higher in the stubble than in the fallow plots at both sites suggesting that residues influenced the amount of N denitrified. Incomplete recovery of ^{15}N in the total-N analysis indicates that losses from the Breton soil occurred in the late fall between addition of the NO_3^- in mid-October and the first sampling in mid-November (Table 12). Losses continued to take place over the winter-spring transition from November to January. There was no discernible loss of ^{15}N from the Breton soil between the January sampling and the final sampling in May. Losses of ^{15}N attributable to denitrification in the Malmo fallow soil occurred in the late fall and between March and May (Table 14). In the Malmo stubble soil losses took place during the late fall and again during the winter-spring transition, March to May. Similar losses of fall-applied NO_3^- attributed to denitrification have been reported in Alberta by Bole *et al.* (1984), Malhi (1978), Malhi and Nyborg (1983b) and in Wisconsin by Chalk *et al.* (1975). Malhi and Nyborg (1983b) proposed that denitrification in the early spring, while the soil surface is saturated and drainage impeded by frost in the lower reachs of the profile, is the major mechanism responsible for overwinter loss of N fertilizers. The results of the present study indicate that NO_3^- was lost from the soil system apparently through denitrification between October and May. Large denitrification losses occurred in the late fall in both the Breton and Malmo soils. Denitrification losses also took place over the fall-winter and winter-spring transitions but their occurrence was variable with soil and treatment. There was no evidence of denitrification losses from the Breton and Malmo soils between January and March while the soil was deeply frozen.

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[1] Depth of snowcover divided by 7.5 equals liquid moisture equvalent, Ferguson and Pollack (1971)

Summary: Experiment 1980B

The results of Experiment 1980B permit distinctions to be drawn between transfers from the mineral-N pool through the internal N cycle and losses from the soil system. Losses from the system due to denitrification were from 2 to 22 times greater than removal through immobilization when the N was added as labelled NO_3^-. Losses of ^{15}N from the zone of application due to leaching were from one to two orders of magnitude less than either denitrification or immobilization and were therefore, in the particular year in which this experiment was carried out, negligible.

Net positive changes in mineral-N while the soil was frozen indicate that processes augmenting mineral-N levels are active during the winter. Increases in the NH_4^+ as well as the NO_3^- pool suggest that mineralization may have been partly responsible for the increase. More dramatic net changes in mineral-N were observed following the winter-spring transition. The N accumulating in the Breton soil was thought to arise mainly through mineralization of previously occluded organic-N which had been released through freeze-thaw disruption of soil aggregates. Conversly, the data suggest that similiar gains in the mineral-N levels of the Malmo soil arose mainly through mineralization of N from biomass killed by freeze-thaw cycles in the spring.

C. EXPERIMENT 1981A: DYNAMICS OF SOIL N LABELLED WITH ^{15}N IN THE FALL OF THE PREVIOUS YEAR

Nitrogen immobilized in soil organic matter is contained in four phases: biomass N, necromass N or recently deposited residues, stabilized N, and recalcitrant N (Jansson and Persson, 1982). At the onset of sampling for experiment 1981A, twelve months had passed since the ^{15}N was first added to the soil as NO_3^-. Following the ideas of Paul and Juma (1981), ^{15}N, not lost to denitrification during the initial year of field incubation, would be contained largely in the biomass and necromass. The four phase system can thus be simplified to two fractions: N immobilized in the preceeding year which contains the ^{15}N label and N immobilized prior to the addition of the label, i.e. older than one year. The source of N entering the mineral-N pool can be indentified by measuring changes in the ^{15}N atom abundance over time. An increase in ^{15}N atom abundance over time occurs if N entering the mineral-N pool is from a highly enriched source whereas a dilution of the isotope reflects a source that has not incorporated ^{15}N.

Results: Experiment 1981A

Changes in the size and ^{15}N atom abundance of the mineral-N pool followed similar trends in the Breton and Malmo soils (Tables 18, 19). The initial level of enrichment measured in December reflects residual ^{15}N from the NO_3^- source and ^{15}N immobilized and then

Table 18. Nitrogen dynamics of a Breton soil treated with ^{15}N as NO_3^- in the fall of the previous year.

N form		Sampling date[1]			
		December	January	March	May
NH_4^+	(μg N/g)	10.8 a	6.9 b	10.4 a	3.1 c
	% At Ab	0.369 b	0.377 a	0.371 b	0.377 a
	% Excess	0.001 b	0.009 a	0.003 b	0.009 a
NO_3^-	(μg N/g)	3.3 b	3.3 b	4.3 a	2.3 c
	% At Ab	0.423 b	0.479 a	0.417 b	0.408 b
	% Excess	0.055 b	0.111 a	0.049 b	0.040 b
Mineral-N	(μg N/g)	14.1 a	10.2 b	14.7 a	5.4 c
	% At Ab	0.382 b	0.410 a	0.384 b	0.390 b
	% Excess	0.014 b	0.042 a	0.016 b	0.022 b
Organic-N	% At Ab	0.372 a	0.372 a	0.372 a	0.371 b
	% Excess	0.004 a	0.004 a	0.004 a	0.003 b

[1] Values in rows are significantly different if followed different letters (LSD, $p=0.05$).

Table 19. Nitrogen dynamics of a Malmo soil treated with ^{15}N as NO_3^- in the fall of the previous year.

N form		Sampling date[1]			
		December	January	March	May
NH_4^+	(μg N/g)	11.6 a	6.5 b	12.3 a	4.2 c
	% At Ab	0.380 b	0.392 a	0.381 b	0.393 a
	% Excess	0.013 b	0.024 a	0.014 b	0.025 a
NO_3^-	(μg N/g)	6.9 a	6.8 a	7.6 a	5.5 a
	% At Ab	0.511 b	0.568 a	0.505 b	0.505 b
	% Excess	0.144 b	0.200 a	0.138 b	0.138 b
Mineral-N	(μg N/g)	18.5 a	13.3 b	19.9 a	9.7 b
	% At Ab	0.429 c	0.482 a	0.428 c	0.457 b
	% Excess	0.062 c	0.102 a	0.061 c	0.089 b
Organic-N	% At Ab	0.380 a	0.379 ab	0.378 b	0.378 b
	% Excess	0.013 a	0.012 ab	0.010 b	0.010 b

[1] Values in rows are significantly different if followed by different letters (LSD, $p=0.05$).

mineralized during the pretreatment period. Changes in the size of the mineral-N pool were greatest in the NH_4^+ fraction; NO_3^- levels remained relatively steady between November and May. During the fall-winter transition (December compared to January) the amount of N in the mineral-N pool declined indicating that transfers out of the pool were taking place. The increase in isotope abundance during this same period shows that N was also entering the mineral-N pool and that these additions were from a labelled source. A similar trend is evident over the winter-spring transition (March *vs* May).

During the mid-winter period, January to March, mineral-N levels rose 4.5 μg N/g in the Breton soil and 6.6 μg N/g in the Malmo soil. This rise in mineral-N was accompanied by a dilution of the ^{15}N label, -0.026% and -0.041% ^{15}N atom abundance in the Breton and Malmo soils respectively. These results indicate that a large portion of the N entering the mineral-N pool arose from a source which had not incorporated the label.

Discussion: Experiment 1981A

Sources and mechanisms of N release active during transitional periods

The increase in the ^{15}N atom abundance of the mineral-N pool during the transition from the unfrozen to the frozen phase implies that the balance between mineralization from labelled and unlabelled sources has shifted towards the former. The possible deleterious effects of freeze-thaw cycles during transitional periods on soil microflora and aggregate stability have been outlined in detail under the discussion of Experiment 1980B. Two explanations of the results are possible. In the first instance, ^{15}N was released into the mineral-N pool as a result of biomass death and subsequent utilization of the N containing metabolites by surviving biomass. This line of reasoning follows the hypothesis forwarded by Campbell (1978). The amount and ^{15}N atom abundance of biomass N was determined by chloroform fumigation on samples collected from the field in November, just prior to the onset of the field experiment. The ^{15}N atom abundance of the biomass was 0.3993% in the Breton and 0.4378% in the Malmo soil (N.G. Juma and B. Mary, unpublished data). In both the Breton and Malmo soils the ^{15}N

atom abundance of mineral-N in December is higher than the enrichment of the biomass. Nitrogen mineralized from the biomass between December and January would tend to decrease the ^{15}N enrichment of mineral-N rather than increase it. Therefore, N entering the mineral-N pool must have arisen from an organic fraction with a higher enrichment than the biomass and the ^{15}N label is not homogeneously distributed within the active N fraction.

A possible source of N with a higher ^{15}N enrichment than the biomass is organic-N occluded within soil aggregates. Freeze-thaw cycles may break down soil aggregates and release previously occluded substrate into the available pool (Alexander, 1977). Utilization of the substrates by the microbial populations in turn releases ^{15}N formerly trapped in aggregates into the mineral-N pool. The ^{15}N entering the mineral-N pool, in accordance with this latter hypothesis, would have been incorporated into the biomass soon after addition of the highly labelled NO_3^- source to the soil the previous year. During the time between initial immobilization and the January sampling, the ^{15}N would have been released as organic-N upon the death of the immobilizing organisms, occluded within soil aggregates, and finally mineralized when the aggregates were disrupted by freeze-thaw cycles. The timing of this sequence is not unlikely. Paul and Juma (1981) found in a Weirdale loam incubated at field capacity moisture and 28 °C that biomass N cycled rapidly with a half life of 24.8 weeks. Similarily, the formation and destruction of soil aggregates is a highly dynamic process. Aggregate turnover time, measured by decomposition of the polysaccharide and polyuronide binding agents, has been reported to occur in time spans of three to twelve months (Martin and Richards, 1963; Martin *et al.*, 1965, 1966).

In the Malmo soil, the size of the mineral-N pool declined by 10.2 μg N/g between March and May indicating that transfers out of the pool were taking place. Over this same time, the ^{15}N atom abundance of mineral-N rose from 0.428% to 0.457% (Table 19). The abundance in May is higher than the abundance of the biomass (0.438%). This result suggests that, in a manner analogous to the fall-winter transition, N entering the mineral-N pool as the Malmo soil thawed and dried is arising from labelled sources other than the biomass. In the

Breton soil, the decline in the size of the mineral-N pool from March to May (14.7 to 5.4μg/g) shows that N was leaving the pool. The ^{15}N atom abundance of mineral-N in March and May (0.384% and 0.390%) are not significantly different (Table 18). There is, therefore, no trend to indicate if N was entering the mineral-N pool between March and May and if so from what sources.

During the periods of transition from the unfrozen to frozen phase, or *vice versus*, mineral-N levels in the Breton and Malmo soils underwent a net decline. The transfers of N out of the pool were accompanied by an influx of N arising from a portion of the active fraction with a greater ^{15}N atom abundance than the biomass. The incoming N was immobilized shortly after the addition of the label and protected from the mainstream of mineralization/immobilization turnover. The results suggest that mineralization of this highly labelled fraction was induced by the change in phase as the soil froze or thawed.

Sources and mechanisms of N release active during mid-winter

The increase in mineral-N observed between January and March and the accompanying dilution of the isotope abundance indicates that a large portion of the N entering the pool during mid-winter is from sources which did not incorporate the ^{15}N label. Four sources are possible: recalcitrant organic-N, stabilized organic-N, fixed NH_4^+, and NO_3^- moving up the profile from below. Campbell and Biederbeck (1982) attributed NO_3^- accumulation in the surface layer of frozen soils in Saskatchewan to the formation of ice lens at the surface inducing liquid flow of NO_3^- containing solution from below. While a similiar phenomenon may have contributed to the dilution of the ^{15}N label contained in the NO_3^- pool, it does not explain the concurrent increase in the amount of N and dilution of ^{15}N in the NH_4^+ pool.

Nitrogen was entering the NH_4^+ pool between January and March, either through release of fixed NH_4^+ or mineralization of unlabelled organic-N. Several factors are against the latter being the sole source of incoming NH_4^+. Samples collected in November 1981, just prior to the commencement of the field experiment, were incubated in the laboratory for three weeks at

20°C. The ^{15}N atom abundance of mineralized N was 0.394% and 0.445% for the Breton and Malmo soils respectively (N.G. Juma and B. Mary, unpublished data). The above values are substantially higher than the mineral-N abundances observed in March in the field (0.384% and 0.428% in the Breton and Malmo soils respectively). Mineralization from the recalcitrant or stabilized N fractions is normally accompanied by a turnover of N in the biomass (Paul and Juma, 1981; Campbell, 1978). Assuming that N biologically mineralized in the field during mid-winter would arise from the younger labelled and older unlabelled fractions in similar proportions to N mineralized in the laboratory, NH_4^+ released by mineralization could not have reduced the ^{15}N atom abundance of mineral-N to the extent observed in the field.

The above point can be further illustrsted by the application of dilution principles. The amount of incoming N required to affect the dilution of the ^{15}N observed between January and March can be described by the following equation:

$$R_1N_1 + R_2N_2 = R_3(N_1+N_2)$$

R_1 = ^{15}N atom abundance of mineral-N in January (%)

R_2 = ^{15}N atom abundance of incoming mineral-N (%)

R_3 = ^{15}N atom abundance of mineral-N in March (%)

N_1 = amount of mineral-N in January (μg N/g)

N_2 = amount of incoming mineral-N (μg N/g)

The values of R_1, R_3 and N_1 are given in Tables 18 and 19 for the Breton and Malmo soils. These values have been used to estimate the amount of incoming N necessary to dilute the label from the levels found in January to those found in March. Estimations have been made using a range of proportional contributions by the labelled and unlabelled organic-N fractions to the N required for dilution. These estimates were then compared to data obtained in the laboratory and from the literature and by this method the feasibility of incoming N having arisen through mineralization was evaluated.

Several assumptions were necessary. Losses from the mineral-N pool between January and March were ignored. The amount of soil organic-N which contains the label (i.e. the active fraction composed of biomass and recent residues) was calculated from the following equation using organic-N data from this study (1495 μg organic-N/g, 0.004% ^{15}N excess and 4686 μg organic-N/g, 0.012% ^{15}N excess; Breton and Malmo soils respectively) in conjunction with the ^{15}N excess of N released during incubation in the laboratory (0.026% for the Breton and 0.078% for the Malmo soil).

$$\text{Active fraction}(\mu\text{g N/g}) = \frac{\text{total organic-N}(\mu\text{g N/g}) \times {}^{15}\text{N excess total organic-N}(\%)}{{}^{15}\text{N excess N mineralized during incubation}}$$

?

The size of the active fraction was estimated at 230 μg N/g for the Breton soil and 721 μg N/g for the Malmo soil. These values are equal to 15.4% of total organic-N for both the Breton and Malmo soil. Jansson (1958) and Paul and Juma (1981) reported that the active fraction consisting of biomass and recently deposited organic debris accounted for 10 to 15% of organic-N. Tables 20 and 21 show the ^{15}N atom abundance of mineralized N (R_2) over a range of proportional contributions for the labelled active and unlabelled active stabilized and recalcitrant fractions and the amount of N necessary at each proportion to affect the dilution to the levels observed in March (N_2).

In the Breton soil, the amount of N required to dilute the mineral-N pool between January and March, even when there was no labelled fraction contribution, is as high as the amount of N mineralized over a similar time period at 20°C in the laboratory. Breton soil obtained from the field in November accumulated approximately 20 μg N/g over 12 weeks of incubation. Of this amount 18% of the N and 27% of the ^{15}N arose from the labelled biomass alone (N. G. Juma and B. Mary, unpublished data). These results indicate that a relatively large portion (73%) of ^{15}N mineralized came from the non-biomass portion of the labelled fraction and that this fraction made a large contribution to the remaining 82% of N mineralized. In the estimations presented in Table 20, it is only in the 20% and below range of active fraction contribution that the amount of N mineralized falls within the range of values comparable to those found in the laboratory at 20°C.

Table 20. Amount of N arising from mineralization necessary to dilute the ^{15}N atom abundance of mineral-N pool between January and March over a range of contributions by labelled vs unlabeled sources in a Breton soil.

Contribution			
Unlabelled[1] organic-N (%)	Labelled[2] organic-N (%)	% At Ab mineralized NH_4^+ (%)	N required for dilution (μg N/g)
20	80	0.389	—
30	70	0.386	—
40	60	0.383	265
50	50	0.381	88
60	40	0.378	44
70	30	0.376	32
80	20	0.373	24
90	10	0.370	19
100	0	0.368	17

[1] ^{15}N atom abundance of unlaballed organic-N, 0.368%.

[2] ^{15}N atom abundance of laballed organic-N, 0.394% (N.G. Juma and B. Mary, unpublished data).

Table 21. Amount of N arising from mineralization necessary to dilute the ^{15}N atom abundance of mineral-N pool between January and March over a range of contributions by labelled vs unlabeled sources in a Malmo soil.

Contribution Unlabelled[1] organic-N (%)	 Labelled[2] organic-N (%)	% At Ab mineralized NH_4^+ (%)	N required for dilution (µg N/g)
20	80	0.437	—
30	70	0.429	—
40	60	0.420	90
50	50	0.411	42
60	40	0.402	28
70	30	0.393	21
80	20	0.385	17
90	10	0.376	14
100	0	0.367	12

[1] ^{15}N atom abundance of unlaballed organic-N, 0.367%.

[2] ^{15}N atom abundance of laballed organic-N, 0.455% (N.G. Juma and B. Mary, unpublished data).

Literature values for contribution of the active fraction including biomass to total N mineralized fall within the range of 50 to 70% (Campbell, 1978; Paul and Juma, 1981). Within this range the amount of mineralized N necessary to affect dilution in the Breton soil, 22 to 101 μg N/g, suggests that mineralization is not a major contributor to dilution of the pool. Furthermore, the comparison presented above is between a frozen soil in the field and a soil in the laboratory at 20°C. If the constraints of temperature on biological activity are considered along with the discussion of active fraction contribution; then the possibility of N entering the mineral-N pool arising from mineralization alone appears rather remote.

In the case of the Malmo soil, 50 μg N/g were mineralized over 12 weeks of laboratory incubation at 20°C with 47% of the mineralized N and 72% of the ^{15}N arising from the biomass (N.G. Juma and B. Mary, unpublished data). Estimates using labelled fraction contributions in the 30 to 60% range fall between 21 and 90 μg N arising from mineralization required to affect the dilution of the mineral-N pool observed between March and May (Table 21). Mineralization rates decline exponentially with temperature with a Q_{10} of approximately 2 (Kai *et al.*, 1969, Stanford *et al.*, 1973). Assuming soil temperature was close to 0°C between January and March, the amount of N mineralized over 12 weeks would 1/4 of that mineralized at 20°C or approximately 12 μg/g. This estimate suggests that mineralization may have made a greater contribution to dilution of the mineral-N pool in the Malmo than in the Breton soil. However, N would not have been mineralized in sufficient quantities to reduce the ^{15}N atom abundance of mineral-N to the extent observed between January and March.

Summary: Experiment 1981A

In the Breton and Malmo soils used in Experiment 1981A, N entering the mineral-N pool during the transition to or from the frozen state appears to arise from organic-N sources which are to some degree protected from biomass use during the remainder of the year. Physical removal from the mainstream of mineralization/immobilization turnover through inclusion of organic-N in soil aggregates and subsequent release through freeze-thaw disruption of the aggregates is suggested by this result.

Mineral-N accumulated between January and March while the Breton and Malmo soils were frozen. Changes in the ^{15}N atom abundance during the frozen period suggest that N entering the mineral-N pool could not have arisen from biological mineralization alone. It has been postulated that release of NH_4^+ from the non-exchangeable pool (W.B. McGill, personal communication) or upward movement of NO_3^- from subsurface horizons may also be contributors to mineral-N build ups (Campbell and Biederbeck, 1981; Campbell *et al.* 1970b). While the data at hand lead to the conclusion that processes other than mineralization are also acitve, further work is necessary before these processes can be positively identified and the extent of their possible contribution measured.

D. EXPERIMENT 1981B: EFFECTS OF BARLEY RESIDUES ON THE DYNAMICS OF MINERAL-N BETWEEN NOVEMBER AND MAY

Experiment 1981B was conducted to determine if the incorporation of residues altered the balance between mineralization/immobilization and denitrification during the fall to spring period and if so, did they have a significant effect on overwinter losses of mineral-N.

Results: Experiment 1981B

Changes in NH_4^+ and NO_3^-

Net changes in NH_4^+ followed similiar trends in the amended and non-amended plots (Table 22). Ammonium-N decreased between December and January, rose as the winter progressed until late March, and decreased over the spring thaw, March to May. Nitrate-N levels remained constant in both amended and non-amended plots between the initial sampling in December and late March. In the Malmo soil, NO_3^- was maintained at a higher level in the non-amended compared to the amended plots. The Breton and Malmo soils showed a net loss of NO_3^- over the winter-spring transition, March *versus* May, under both residue amended and non-amended treatments. *Overwinter dynamics of ^{15}N*

Comparing total ^{15}N recovery in December to the amount originally added shows that late fall losses occurred in both the amended and non-amended Malmo soil (Tables 23 and 24). Total losses were higher, averaging 63.3%, in the plots that recieved residues than in those that did not, 46.7% loss. In the Breton soil, 52.5% of applied N was lost from the non-amended treatment. Recovery in December was complete in residue amended plots. The ^{15}N remaining in the system at the December sampling date was largely in NO_3^- and organic-N. The amount of ^{15}N immobilized in the organic-N fraction was higher in the amended plots of both soils. A small amount of ^{15}N was detected in the NH_4^+ pool at the December sampling, indicating that late fall mineralization of organic-N was taking place.

During the fall-winter transition, the one month period from December to January, ^{15}N recovery in the organic-N fraction declined under both treatments (Tables 23 and 24). The losses of ^{15}N from the organic-N fraction were statistically significant in the amended but not the non-amended plots. Total recovery of ^{15}N declined between December and January in both the residue amended and non-amended plots of the Breton and Malmo soils. The loss of ^{15}N from the system was not large enough to be statistically significant in the non-amended Breton soil. Recovery of ^{15}N as NO_3^- remained constant between December and January in all plots.

From January to March there was a slight decrease in the recovery of total ^{15}N. The decrease was only significant in the amended plots of the Breton soil. There was also a significant decrease in the amount of ^{15}N recovered in the organic-N and NO_3^- fractions of the amended Breton soil. In the Malmo soil, recovery of ^{15}N tagged fertilizer as NO_3^- declined significantly in the non-amended plots during this same period.

In May, the recovery of residual ^{15}N as NO_3^- was substantially lower than in March in all plots; however, the partitioning of N leaving the NO_3^- pool differed between treatments. The decline of ^{15}N as NO_3^- in the non-amended plots was equal to the the loss of ^{15}N from the soil system during the winter-spring transition. In contrast, ^{15}N leaving the NO_3^- pool in the amended plots was partitioned, approximately two thirds to one third, between immobilization into the organic-N fraction and losses from the soil system presumably through denitrification.

Table 22. Fall through spring changes in NH_4^+ and NO_3^- in two soils with and without additions of barley residues.

Sampling date	Amount of N (0-15 cm)[1] (μg N/g)			
	NH_4^+		NO_3^-	
	residue	none	residue	none
Breton soil				
December	10.4 Aa	11.2 Aa	4.4 Aa	5.4 Ba
January	7.5 Ba	7.5 Ba	4.9 Aa	4.9 Ba
March	9.8 Ab	11.3 Aa	4.1 Ab	6.5 Aa
May	5.5 Ca	3.2 Cb	0.9 Bb	2.3Ca
Malmo soil				
December	10.6 Bb	11.7 Aa	4.3 ABb	9.8 Aa
January	8.1 Ca	6.7 Bb	4.8 Ab	10.0 Aa
March	13.0 Aa	11.5 Ab	5.2 Ab	8.8 Aa
May	6.0 Da	3.4 Cb	3.0 Ba	4.6 Ba

[1] Values in columns are statistically different if followed by different upper case letters; values for residues vs none at each sampling date are statistically different if followed by different lower case letters (LSD, $p=0.05$).

Table 23. Overwinter changes in the ^{15}N content of NH_4^+, NO_3^-, organic-N, and total-N fractions in two soils with and without additions of barley residues[1].

Sampling date	Recovery of ^{15}N fertilizer (0-15 cm)[2] (μg N x 10^{-2}/g)[2].							
	NH_4^+		NO_3^-		Organic-N		Total-N	
	residue	none	residue	none	residue	none	residue	none
				Breton soil				
December	4.9 Aa	1.5 Ab	125 ABb	200 Aa	417 Aa	46 Ab	546 Aa	248 Ab
January	2.0 Ba	0.8 Bb	162 Aa	198 Aa	206 Ba	23 Ab	370 Ba	222 Ab
March	2.2 Ba	0.5 BCb	100 Bb	179 Aa	106 Ca	28 Ab	208 Ca	208 Aa
May	0.8 Ca	0.2 Cb	1 Ca	5 Ba	180 Aa	16 Ab	182 Ca	21 Bb
				Malmo soil				
December	1.4 Aa	1.0 Aa	92 Ab	269 Aa	119 Aa	38 Ab	212 Ab	308 Aa
January	0.5 Ba	0.5 ABa	99 Ab	234 Aa	37 Ca	12 Aa	136 Bb	246 Ba
March	1.2 Aa	0.5 ABb	80 Ab	184 Ba	45 Ca	19 Aa	126 Bb	204 Ba
May	1.8 Aa	0.2 Bb	24 Ba	25 Ca	88 Ba	18 Ab	114 Ba	43 Cb

[1] Fertilizer N added as NO_3^- at a rate of 5.21 μg N/g and 5.78 μg N/g to the Breton and Malmo soils respectively, November 1981.

[2] Values in columns are statistically different if followed by different upper case letters; values for residues vs none at each sampling date are statistically different if followed by different lower case letters (LSD, $p=0.05$).

Table 24. Percent recovery of ^{15}N enriched fertilizer in various fractions of a Breton and a Malmo soil, November 1981 to May 1982 (0-15 cm).

Form of N	Treatment	Recovery of ^{15}N fertilizer[1]							
		December		January		March		May	
		%	d %[2]	%	d %[2]	%	d %[2]	%	d %[2]
		Breton soil							
NH_4^+	residue	0.9	0.9	0.4	-0.5	0.4	0.0	0.2	-0.2
	none	0.3	0.3	0.2	-0.1	0.1	-0.1	0.0	-0.1
NO_3^-	residue	23.4	-76.6	31.0	7.6	19.1	-11.9	0.20	-18.9
	none	38.4	-61.6	37.9	-0.5	34.4	-3.5	1.0	-33.4
Organic-N	residue	80.0	80.0	39.5	-40.5	20.0	-19.5	34.5	14.5
	none	8.8	8.8	4.4	-4.4	5.4	1.0	3.0	1.4
Total-N	residue	104.3	4.3	70.9	-33.4	39.5	-31.4	34.8	-4.7
	none	47.5	-52.5	42.4	-5.1	39.9	2.5	4.0	-35.9
		Malmo soil							
NH_4^+	residue	0.2	0.2	0.1	-0.1	0.2	0.1	0.3	0.1
	none	0.2	0.2	0.1	-0.1	0.1	0.0	0.0	-0.1
NO_3^-	residue	15.9	-84.1	17.1	1.2	13.8	-3.3	4.2	-9.6
	none	46.5	-53.5	40.5	-6.0	31.8	-8.7	4.3	-27.5
Organic-N	residue	20.6	20.6	6.4	-14.2	7.8	1.4	15.2	7.4
	none	6.6	6.6	2.1	-4.5	3.4	1.3	3.1	-0.3
Total-N	residue	36.7	-63.3	23.6	-13.1	21.8	-1.8	19.7	-2.1
	none	53.3	-46.7	42.7	-10.6	35.3	-7.4	7.4	-27.9

[1] Fertilizer N added as NO_3^- at a rate of 5.21 μg N/g and 5.78 μg N/g to the Breton and Malmo soils respectively, November 1981.

[2] Change in % of fertilizer N recovered in each fraction from the previous sampling date.

Recovery of ^{15}N in samples obtained in May from the 15-30 and 30-45 cm depths ranged from 3.2 x $10^{-2}\mu g^{15}N/g$ to 5.3 x $10^{-2}\mu g^{15}N/g$. In all cases, the amount of ^{15}N recovered below the zone of application was less than 1% of the ^{15}N added in November.

Discussion: Experiment 1981B

Effects of residues on soil N dynamics in the late fall

During the 10 day period between addition of the ^{15}N label and the December sampling, immobilization of NO_3^- in the amended plots accounted for 80.8% of the N added to the Breton soil and 20.6% of the N added to the Malmo soil. Residues enhanced immobilization of ^{15}N 9 fold in the amended Breton soil and 3 fold in the amended Malmo soil compared to the non-amended treatment. The greater immobilization of ^{15}N in the amended Breton plots suggests that carbon limitations on the biomass were more pronounced in the Breton soil (Tables 23 and 24).

In the Malmo soil, the amount of NO_3^- present in December was lower in the amended (4.3 μgN/g) than in the non amended plots (9.8 μgN/g) (Table 22). Additions of N to the NO_3^- pool could not keep pace with the rapid removal of N induced by the the residues. At Breton, there was no substantial difference between NO_3^- levels of the two treatments in the December sampling (4.4 μgN/g *vs* 5.4 μgN/g) even though the net immobilization rate was 9 times higher in the amended plots. Nitrate immobilized in the amended plots at Breton was apparently rapidly replaced by incoming NO_3^- arising from mineralization. It would seem likely that in the Breton soil the addition of residues stimulated mineralization/immobilization turnover to a greater extent than in the Malmo soil.

In addition to stimulating late fall immobilization, the addition of residues appeared to increase late fall denitrification in the Malmo soil. A total of 366 x $10^{-2}\mu g^{15}N/g$ was irrecoverably lost from the the residue amended plots prior to the December sampling, 63.3% of the ^{15}N added ten days earlier. Losses from the non-amended plots were somewhat less, 270 x $10^{-2}\mu g^{15}N$ or 46.7% of added ^{15}N. In the Breton soil, recovery of the ^{15}N was complete in the residue amended plots but 273 x $10^{-2}\mu g^{15}N/g$ or 52.5% of the added ^{15}N was lost from the non-amended plots.

The apparent difference in the way the two soils behaved in the late fall may be due to a number of reasons. Possibly immobilization proceeded denitrification in time at Breton, i.e.—most of the added ^{15}N in the residue amended plots was incorporated into the biomass prior to the onset of denitrification. If this were the case then denitrification losses from the the amended plots would have gone largely undetected because the label had already left the NO_3^- pool. Conversely, addition of residues to the Breton soil may have created conditions under which assimilatory reduction of NO_3^- into the biomass took precedence over dissimilatory reduction through denitrification. In the amended plots, one can envision a series of carbon rich microsites forming in the vicinity of the residue particles. Islands of intense microbial activity surrounded by the ^{15}N evenly dispersed in the soil solution. These microsites would subsequently become strong immobilizing sinks for solution NO_3^-, preventing denitrification by out competing the denitrifying organisms for substrate.

The preceeding hypothesis supports the idea the available carbon was strongly limiting biomass growth and N immobilization in the Breton soil. However, the loss of ^{15}N from the non-amended plots demonstrates that the Breton soil posessed a significant denitrification potential and that while carbon may have been limiting immobilization it was not limiting denitrification to as great an extent. This observation leads to speculation on the spatial distribution of available carbon in the Breton soil. Were the aerobic environs within the Breton soil relatively bereft of carbon while within the anaerobic confines of aggregate interiors carbon was available. In keeping with this latter idea, solution NO_3^- could have followed two diffusional pathways within the soil. One leading into the anaerobic microsites that Greenwood (1961, 1975) has suggested exist in the center of soil aggregates and the other leading to the sites of intense microbial activity surrounding the particles of residues. In the residue amended plots in the Breton soil, the immobilization of N may have been so rapid that NO_3^- flow followed the latter pathway almost exclusively resulting in no measurable loss through denitrification.

The immobilization of ^{15}N was increased and denitrification circumvented in the Breton soil by the addition of available carbon in the form of residues but not in the Malmo soil. This observation implies that energy was limiting biomass growth and N immobilization, but not denitrification. Immobilization of ^{15}N was close to complete once energy restraints were removed from the biomass in the Breton soil. In the Malmo soil, some factor other than available energy was or became the limitation on immobilization of N. Incomplete immobilization left NO_3^- available for denitrification and residues enhanced the rate of NO_3^- loss. In summary, the effects of added residues during the 10 days in late fall between addition of the residues and the initial sampling were variable. Residues prevented dinitrification in the Breton soil and increased them in the Malmo soil.

Nitrogen dynamics of amended vs non-amended plots in winter

Nitrogen-15 levels in the organic-N fraction declined significantly from December to January in all but the non-amended plots of the Breton soil (Table 23). Nitrogen originally immobilized in the late fall appeared to be mineralized over the fall-winter transition. This observation is consistent with the results of Experiment 1981A in which changes in the ^{15}N enrichment of the mineral-N pool pointed to a release of previously immobilized N as the soil froze. The trend in NH_4^+ levels in Experiment 1981B was also similiar to the one reported for Experiment 1981A in that NH_4^+ levels declined between December and January. This decline of both ^{15}N and ^{14}N levels indicates that N mineralized from the biomass was not retained as NH_4^+, but either re-immobilized or nitrified. It is of interest that during a period when a great deal of ^{15}N was being released from the biomass, especially in the residue amended plots, a proportionally small amount was recovered as exchangeable NH_4^+. Between December and January, the ratio of ^{15}N to ^{14}N in exchangeable NH_4^+ declined in all plots, suggesting that the ^{15}N released from organic-N was diluted within a large concomitent release of ^{14}N. On the other hand, similiar results would have been obtained if NH_4^+ held within the exchangeable pool did not enter into the mainstream of mineralization/immobilization turnover. If this latter supposition were true, then dilution of the ^{15}N label within the NH_4^+ pool may have been through a selective desorbtion of ^{15}N following a last on first off criteria. Returning to the former case, if dilution of the NH_4^+ pool took place due to the release of organic-N through mineralization, why was this dilution not passed on to the NO_3^- pool. The ratio of ^{15}N to ^{14}N in the NO_3^- pool remained constant in some plots and rose slightly in others. This implies that N entering the NO_3^- pool was of equal or higher ^{15}N atom abundance than the NO_3^- present in December. Following from the above, NH_4^+ held on the cation exchange complex would seem to be outside the mainstream of the organic-N to solution NH_4^+ to NO_3^- conversion sequence.

The ideas presented on the role of exchangeable NH_4^+ in the mineralization sequence are adjunct to the following observations of how residues influenced N behavior during the early winter. In the late fall, a rapid immobilization of N in the organic-N fraction occurred in the plots receiving residues. Much of the N thus immobilized was released from the organic-N pool over the fall-winter transition (December to January). The trend in the non-amended plots, immobilization followed by loss, was similiar in direction but much smaller in magnitude. In the amended plots, the ^{15}N which left the organic-N pool was not quantitatively transferred to either the NH_4^+ or the NO_3^- pool. It was, for the most part, lost from the soil system.

The greater loss of ^{15}N from the residue amended plots suggests that residues increased the denitrification rate between December and January. The difference in denitrification losses from amended *versus* non-amended plots was greater in the Breton than in the Malmo soil. This difference may have been due to available carbon restricting denitrification in the non-amended Breton soil to a greater extent than in its Malmo counterpart.

Total recovery of ^{15}N continued to decline between January and March in the amended Breton and non-amended Malmo plots. The greatest decline was observed in the amended Breton soil; where an average of 31.4% of the ^{15}N labelled fertilizer was lost from the plots (Table 24). This loss was partitioned between a decline in ^{15}N as NO_3^- of 11.9% and a concomitent decline in the organic-N pool of 19.5%. Losses from the non-amended Malmo soil were somewhat smaller, averaging 7.4% of added ^{15}N. There was no significant change in ^{15}N recovery in the non-amended Breton or amended Breton soil.

The dynamics of ^{15}N during the January to March period varied between treatments and between soils. A number of inferences concerning the behavior of N in frozen soils can be drawn from the data. Malhi and Nyborg (1985) postulated that denitrification during the spring thaw was the major mechanism through which fertilizer N was lost from the soil. The results of Experiment 1981B illustrate that overwinter N loss is not restricted to the spring but can occur throughout the fall and winter. In the case of the amended Breton soil, 31.4% of the ^{15}N applied in the fall was lost over the mid-winter period, January to March, while the soil was deeply frozen. Rice *et al.* (1984) have reported denitrification losses from soils incubated at -4°C in the laboratory. The data at hand support the idea that denitrification can and does on occasion occur in frozen soils in the field as well as the laboratory.

Mid-winter build up of mineral-N levels in soil have been reported previously by Malhi and Nyborg (1985). The mechanism or mechanisms by which N enters the mineral-N pool has, however, not been satisfactorily explained to date. Under the discussion of Experiment 1981A, the present author suggested that N entering the mineral-N pool could not be the product of mineralization alone. The results from the experiment currently under discussion, in which the level of ^{15}N within the organic-N fraction declined between January and March, suggest that mid-winter mineralization can occur in some soils. Mid-winter increases in the mineral-N content, in light of these findings, are b[illegible] viewed as arising through a mixture of mechanisms. One of which can be mineralization and the rest of which are as yet undefined. Also undefined are the variables which control the contribution each mechanism makes to the total release in minearal-N.

Nitrogen dynamics during the winter-spring transition

Between March and May, the size of the mineral-N pool declined in both the Malmo and Breton soil. Net decline of NH_4^+ as well as NO_3^- took place in all plots (Table 22). The decline in mineral-N levels indicates that mechanisms of mineral-N addition were outweighed by mechanisms of removal. In the case of NH_4^+, immobilization, nitrification or a combination of the two may have been decreasing the size of the pool. The amount of ^{15}N within the NH_4^+ pool declined significantly in the Breton but not the Malmo soil between March and May; however, the amount of ^{15}N transferred out of the NH_4^+ pool was too small to be detected against the high ^{15}N atom abundance the organic-N and NO_3^- fractions. Thus, the partitioning of NH_4^+ flow between immobilization and nitrification cannot be calculated from the data.

The data provide a somewhat clearer picture of the fate of N leaving the NO_3^- pool. The level of ^{15}N recovered as NO_3^- declined sharply, regardless of treatment, in both soils over the winter-spring transition. Of the possible pathways of NO_3^- removal; leaching, immobilization, and denitrification; leaching losses were least significant. In the Malmo soil, 3.6 x $10^{-2}\mu g^{15}N/g$ and 3.9 x $10^{-2}\mu g^{15}N/g$ was recovered from the 15-30 cm depth under the amended and non-amended plots respectively. Recovery of ^{15}N from the 30-45 cm depth at Malmo was nil. Similiar low recoveries, 3.2 x $10^{-2}\mu g^{15}N/g$ under the amended plots and 5.0 x $10^{-2}\mu g^{15}N/g$ under non-amended plots, were obtained from the 15-30 cm depth of the Breton soil. An additional 2.1 x $10^{-2}\mu g^{15}N/g$ was recovered from the 30-45 cm depth under the amended plots. There was no recovery below 30 cm in the non-amended plots.

In the amended Malmo soil, movement down the profile accounted for only 6.8% of the ^{15}N transferred out of NO_3^- pool of the 0-15 cm depth between March and May. A smaller percentage, 2.5% was moved down the profile under the non-amended plots. Percentage losses were similiar in the amended Breton soil, 5.5 % of the ^{15}N present as NO_3^- in March was recovered below 15 cm in May. In the non-amended plots, 2.9% of the ^{15}N as NO_3^- was recovered in the 15-45 cm layer in May. As a percentage of the ^{15}N added in November these losses range from 0.6 to 1.1%. As in other experiments reported in this study, spring melt waters did not transport NO_3^- in either quantity or distance down the profile. With respect to partitioning of losses between immobilization and denitrification the fate of ^{15}N leaving the NO_3^- pool from March to May differed with treatment. In the non-amended plots of the Malmo soil, loss of ^{15}N from the soil system was equal to 98% of the loss from the NO_3^- pool.[2] A similiar calculation for the non-amended plots of the Breton soil yields a value of 109% loss. If losses of ^{15}N from the soil system can be construed as losses due to denitrification, then ^{15}N removal from the NO_3^- pools of non-amended plots took place almost exclusively throught the denitrification pathway. Much different results were obtained from the amended plots. In the Malmo soil, only 32% of the ^{15}N leaving the NO_3^- pool was denitrified, while 62% was found immobilized in the organic-N fraction. The corresponding values for the Breton soil were 23% removal through denitrification and 73% through immobilization.

Residues apparently stimulated immobilization of ^{15}N from the NO_3^- pool during the winter-spring transition and thereby prevented ^{15}N loss through denitrification. While this observation is of agronomic significance in itself, of greater interest is why this phenomenon took place. What factors or combination of factors stimulated immobilization to a greater extent than denitrification in the residue amended plots between March and May. Furthermore, did the partitioning of ^{15}N leaving the NO_3^- occur when the immobilization and denitrification pathways were competing for NO_3^- directly, or did immobilization take place prior to denitrification. If the latter were the case, then NO_3^- loss from amended plots through denitrification may have been underestimated in the ^{15}N balance calculated in May. Several hypotheses can be forwarded to explain the behavior of NO_3^- during the winter-spring transition. The surface few centimetres of the soil may have thawed under the snowpack. This in turn may have stimulated the biomass to immobilize NO_3^- during the late winter, with denitrification taking place during a subsequent period as the snowpack melted and the soil became saturated with melt waters. Conversely, immobilizaton and denitrification may have taken place simultaneously during the saturated period which accompanies snowmelt. In this latter circumstance, competition between two metabolically different microbial populations may have controlled the fate of ^{15}N leaving the NO_3^- pool. An available N tug-o-war with NO_3^- respiration by denitrifying bacteria losing two to one to NO_3^- assimilation by a non-denitrifying anaerobic population. Corequisite to the preceeding hypothesis is the further hypothesis that the activity of the assimilatory population was induced by the residues in conjunction with the onset of anaerobic conditions. Similiar ideas have been discussed by Alexander (1977), who points out that large numbers of facultative anaerobes of the genus *Bacillus* and obligate anaerobes of the genus *Clostridium* exist as dormant endospores in the soil. Transformation of endospores to active vegetative cells, as water from snow melt infiltrated the residue amended soil, may have produced a large active anaerobic population capable of assimilating NO_3^-. The NO_3^- thus trapped in the biomass would have been protected from respiratory use by denitrifying bacteria and retained within the soil system.

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[2] Total loss from 0-15 cm layer minus recovery 15-45 cm divided by loss from NO_3^- pool.

The data show that losses of ^{15}N, similiar to those reported in other studies (Malhi, 1978; Malhi and Nyborg, 1979, 1983b), occurred over the winter-spring transition. Denitrification greatly outweighed leaching as a mechanism of N loss. Residues applied in November with the ^{15}N induced immobilization the following spring and thereby partially prevented NO_3^- loss through denitrification.

Summary: Experiment 1981B

Total recovery in May of ^{15}N added in November as NO_3^- was 3 times greater in the amended compared to the non-amended plots of the Malmo soil. In the Breton soil, the difference was more pronounced. Recovery of ^{15}N from amended pl[illegible] outweighed non-amended plots by a factor of 9 to 1. During the late fall and early winter, residues enhanced denitrification as well as immobilization, probably through a general increase in biological activity. As the winter progressed, the enhancement of immobilization ultimately outweighed increases in denitrification and partially prevented denitrification losses during the spring thaw. The net effect of incorporating barley residues was to lower the amount of ^{15}N lost over the winter in both the soils used in this study.

Although residues to an extent prevented N from leaving the soil system, spring recovery of ^{15}N was by no means complete. Losses were extremely high under the amended and non-amended regimes of both soils. Of the 5.78 $\mu g\,^{15}N/g$ added to the Malmo soil in November, only 19.7% was recovered in the amended plots and 7.4% in the non-amended plots the following May. Spring recovery was slightly higher in the amended plots of the Breton soil, averaging 34.8% of applied ^{15}N, but somewhat lower in the non-amended plots where only 4.0% of the added ^{15}N was still detectable within the sampled profile.

V. CONCLUSIONS

Changes in mineral-N levels were observed from fall through spring in all the soils used in this study. This result is in general agreement with the findings of previous studies into the overwinter behavior of native and fertilizer N (Bole *et al.* 1984; Campbell *et al.* 1970b; Malhi 1978; Malhi and Nyborg, 1979, 1982, 1983, 1985; Malhi *et al.* 1984; Kryzanowski *et al.* 1984). While rates of mineral-N gain or loss may vary from soil to soil and from year to year, the available data support the following general conclusion:

1. The flow of N through the mineral-N pool is continuous throughout the fall, winter, and spring in agricultural soils of the Canadian prairies.

With respect to mechanisms removing N from the NO_3-N pool, the ^{15}N data obtained from Experiments 1980B, 1981A, and 1981B showed that leaching, immobilization, and denitrification were all contributing to total overwinter losses. Spring recovery below the zone of application was in all cases less than 1% of the ^{15}N applied as NO_3-N in the fall, suggesting that leaching was the least important mechanism of mineral-N loss. Furthermore, the ^{15}N transported downwards by spring melt waters was deposited at depths well within the rooting zone of most crop species. It was, therefore, potentially recoverable over the subsequent growing season and could not be considered as lost from the soil system at the time the final samples were obtained in May. Rennie *et al.* (1976) pointed out that summerfallowing greatly enhances leaching losses of N by permitting precipitation to penetrate the profile to a greater depth than under crop. From this, one can speculate that NO_3-N initially transferred down the profile in the spring might be leached below the zone of potential root recovery in cases where rain fell on soils under fallow or prior to crop establishment. Leaching, while not a direct mechanism of overwinter N loss in the soils used in this study, may be the first step in leaching losses incurred during the remainder of the year.

The partitioning of N leaving the mineral-N pool between immobilization and denitrification varied considerably between soils, years, and treatments. Immobilization in the biomass can reduce the size of the mineral-N pool. It does not constitute a loss of N from the soil system. The biomass rather acts as a retainer, preventing removal of N by denitrification or leaching. Denitrification, on the other hand, is a direct and irrecoverable loss of N. In the present study, ^{15}N results showed that N was lost from the mineral-N pool between late fall and early spring. A portion of the ^{15}N lost, ranging from 57 to 96% of the ^{15}N applied in the fall, was not recovered as either organic-N or as mineral-N below the zone of application. The above values provide an indirect measure of denitrification and lead to the second conclusion of this study:

2. In the Breton and Malmo soils used in this study, denitrification was the most important mechanism through which mineral-N was lost from the soil between fall and spring.

Malhi and Nyborg (1983b) reached a similiar conclusion, postulating that denitrification, during the early spring while the soil is saturated by snow melt, is the major cause of fall-applied fertilizer N loss. The conclusions of the present study are in general agreement with their statement. Denitrification, however, can occur, based on the ^{15}N studies reported here, throughout the winter and while losses were largest in the late fall and early spring, denitrification losses in mid-winter can make a significant contribution to total loss.

Increases in mineral-N levels during the winter have been previously attributed to movement of NO_3-N up the profile from lower depths (Campbell *et al.* 1970b) and biological mineralization of organic-N (Malhi and Nyborg, 1982). While movement up the profile was not rigorously examined in the current study, certain prerequisites to its occurrence were derived from Miller (1980). In particular, NO_3-N must be present in the lower reachs of the profile. The results from Experiment 1980A show that in all but the Didsbury fallow soil,

NO_3-N levels in the lowest sampling depth (30-60 cm) were less than 10.3 kg N/ha in November and remained relatively constant as the soil froze between the November and January sampling. Furthermore, late fall and winter changes in mineral-N levels, when they were observed, affected the NH_4-N pool as well as the NO_3-N pool. While upward movement of NO_3-N may have taken place as the soil was freezing, its contribution to the overwinter dynamics of mineral-N in the surface horizon was not detectable.

With respect to N entering the mineral-N pool as NH_4-N, the data suggest that different mechanisms of N release were operating during the fall-winter and winter-spring transitional periods compared to mid-winter. In Experiment 1981A, changes in the ^{15}N enrichments of the various N fractions indicated that as the soil was freezing in the fall and thawing in the spring, N was released from a labelled organic-N fraction. Implicit to the interpretation of this trend is involvement of the biomass, either as the source of the ^{15}N mineralized or as the agent of mineralization. Similiarly, in Experiment 1981B, the ^{15}N data suggested a high level of biomass activity during transition to or from the frozen phase. The results of Experiments 1981A and 1981B support the hypothesis that biological mechanisms are mainly responsible for additions to the mineral-N pool during transitional periods.

Mid-winter additions to the mineral-N pool appear to involve additional processes to those mediated by the soil biota. The ^{15}N data from Experiment 1981A is consistent with the idea that NH_4-N release took place from sources other than the organic-N fraction. This second source has been tenitively identified as NH_4-N held in fixed or slowly exchangeable positions. While Experiment 1981A provided evidence implicating processes other than biological mineralization in NH_4-N release, ^{15}N data from Experiment 1981B clearly showed that N immobilized in the organic-N fraction was mineralized during mid-winter. When viewed together the data lead to the third conclusion of this study:

3. Additions to the mineral-N pool of the soils used in this study occurred through a mixture of biological and non-biological mechanisms. Biological processes appeared to dominate during the periods of transition to or from the frozen phase. Physical and/or chemical processes appeared to supplement biological processes during mid-winter when the soil was deeply frozen.

There remains the question of how residues affected the overwinter dynamics of mineral-N. The results of Experiment 1981B suggest that residues increased both denitrification and immobilization during the late fall and winter-spring transition, probably through a general increase in biological activity. Removal of ^{15}N from the NO_3^- pool of residue amended plots was initially higher than from the non-amended plots. The net effect of residues was benificial when ^{15}N recovery in May is compared to the amount added in November. Residues increased ^{15}N recovery within the sampled profile by a factor of 3 in the Malmo soil and 9 in the Breton soil.

The residues used in Experiment 1981B were more finely ground and more thoroughly incorporated than is commonly done in agricultural practice. Consequently, extrapolation of the data from Experiment 1981B to a field scale is somewhat tenuous. In a qualitative sense however, the results lead to the following conclusion:

4. Incorporation of crop residues in the fall will to some degree increase immobilization of mineral-N and thereby reduce denitrification losses between fall and spring.

In central Alberta soils, the processes affecting mineral-N levels are active from fall through spring. Denitrification appears to be the major avenue of overwinter N loss. Leaching losses during the spring appear to be a very minor compared to denitrification. From an agronomic standpoint, the mechanism of N loss is somewhat less important than the extent of N loss. In view of the results of the present study and other studies like it (Bole *et al.* 1984; Malhi and Nyborg, 1979,1983a,1983b, and 1985; Malhi *et al.* 1984), losses outside the growing season occur over a wide of agricultural soils in Alberta and are in all likelyhood a major contributor to the declining fertility of these soils.

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APPENDIX A

List of Equations used in Calculating

^{15}N Fertilizer Recovery

1. Isotope Dilution Equation

$$Ao = \frac{Am(x+y) - Ai(y)}{x}$$

Ao = ^{15}N atom abundance unknown sample (%)

Am = ^{15}N atom abundance in sample plus internal standard mixture (%)

Ai = ^{15}N in internal standard (%)

x = N in sample (μg)

y = N in standard (μg)

2. ^{15}N atom excess

^{15}N atom excess (%) = ^{15}N Atom abundance sample (%) - ^{15}N natural abundance (%)

3. Nitrogen derived from fertilizer (Ndff):

a. $$\text{Ndff (\%)} = \frac{^{15}\text{N atom excess sample (\%)}}{^{15}\text{N atom excess fertilizer (\%)}} \times 100$$

b. $$\text{Ndff} (\mu g) = \frac{\text{\% Ndff} \times \mu g \text{ N sample}}{100}$$

c. Ndff ($\mu g/g$) = Ndff (μg)/df(g)

$$\text{df = dilution factor} = \frac{\text{Extractant (mL)}}{\text{Aliquot (mL)} \times \text{soil weight(g)}}$$

Experiment 1980B : df = 20 g
Experiment 1981A : df = 45 g
Experiment 1981B : df = 45 g

4. Percent Recovery Fertilizer:

$$\text{Recovery (\%)} = \frac{\text{Ndff}(\mu g/g)}{\text{Nfa} (\mu g/g)} \times 100$$

Nfa = fertilizer nitrogen added ($\mu g/g$)

APPENDIX B

Raw ^{15}N Data from Experiments 1980B, 1981A, 1981B.

APPENDIX B: Table 1. Determination of percent atomic abundance of $(NH_4)_2SO_4$ used to dilute samples (Ai).

Replicate No.	Atomic Abundance (%)
1	0.3656
2	0.3659
3	0.3659
4	0.3655
5	0.3657
6	0.3659
7	0.3659
8	0.3658
9	0.3659
10	0.3659
11	0.3659
12	0.3655
13	0.3657
14	0.3657

Mean ± standard deviation = 0.3658 ± 0.0002

Coefficient of variation = 0.055%

APPENDIX B: Table 2. Determination of ^{15}N natural abundance values in various N fractions of a Breton soil.

Form of N	Rep	x (μg)	y (μg)	Am (%)	Ao (%)
NH_4-N	1	95	1000	0.3667	0.3761
	2	134	1000	0.3654	0.3624
	3	75	1000	0.3665	0.3758
	4	267	1000	0.3657	0.3653
	5	253	1000	0.3658	0.3658
	6	123	1000	0.3656	0.3640
				Mean[1]	0.3682 ± 0.0061
NO_3-N	1	1428	nil	0.3724	0.3724
	2	1833	nil	0.3631	0.3631
	3	272	1000	0.3680	0.3761
	4	1571	nil	N/A	0.3643
				Mean[1]	0.3690 ± 0.0063
Total-N	1	1476	nil	N/A	0.3678
	2	1570	nil	N/A	0.3668
	3	1621	nil	N/A	0.3676
	4	1399	nil	N/A	0.3678
	5	1436	nil	N/A	0.3681
	6	1508	nil	N/A	0.3670
	7	1637	nil	N/A	0.3679
				Mean[1]	0.3676 ± 0.0005

[1] Means reported ± standard deviation.

APPENDIX B: Table 3. Determination of ^{15}N natural abundance values in various N fractions of a Malmo soil.

Form of N	Rep	x (μg)	y (μg)	Am (%)	Ao (%)
NH_4-N	1	117	1000	0.3666	0.3734
	2	112	1000	0.3668	0.3757
	3	134	1000	0.3660	0.3675
	4	343	1000	0.3660	0.3666
	5	365	1000	0.3659	0.3662
	6	406	1000	0.3654	0.3644
	7	474	1000	0.3659	0.3661
	8	367	1000	0.3657	0.3654
	9	297	1000	0.3655	0.3645
	10	332	1000	0.3653	0.3638
	11	373	1000	0.3658	0.3658
				Mean[1]	0.3672 ± 0.0038
NO_3-N	1	286	1000	0.3682	0.3766
	2	524	1000	0.3647	0.3626
	3	467	1000	0.3670	0.3696
	4	267	1000	0.3654	0.3639
	5	192	1000	0.3668	0.3720
	6	503	1000	0.3664	0.3676
	7	487	1000	0.3654	0.3646
	8	964	nil	0.3651	0.3651
				Mean[1]	0.3678 ± 0.0048
Total-N	1	1321	nil	N/A	0.3679
	2	1383	nil	N/A	0.3678
	3	1228	nil	N/A	0.3666
	4	1200	nil	N/A	0.3665
	5	1204	nil	N/A	0.3672
	6	1170	nil	N/A	0.3675
				Mean[1]	0.3672 ± 0.0006

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[1] Means reported ± standard deviation.

APPENDIX B: Table 4. Experiment 1980B, Recovery of ^{15}N in NH_4-N fraction of a fallow Breton soil (0-13 cm).

Sampling date	Rep	x (μg)	y (μg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1] (ng)	(ng N/g)
November	1A	78	1000	0.3699	0.4225	0.0543	0.056	46	2.3
	B	74	1000	0.3702	0.4297	0.0615	0.064		
	2A	81	1000	0.3691	0.4098	0.0416	0.043	41	2.0
	B	69	1000	0.3702	0.4340	0.0658	0.068		
	3A	68	1000	0.3686	0.4098	0.0416	0.043	39	2.0
	B	72	1000	0.3703	0.4328	0.0646	0.067		
	Mean[2]	74±5						42±4	2.1±0.2
January	1A	59	1000	0.3683	0.4107	0.0425	0.042	34	1.75
	B	56	1000	0.3699	0.4431	0.0749	0.078		
	2A	55	1000	0.3755	0.5519	0.1837	0.191	159	8.0
	B	69	1000	0.3852	0.6664	0.2982	0.310		
	3A	80	1000	0.3673	0.3860	0.0178	0.018	21	1.0
	B	54	1000	0.3684	0.4165	0.0483	0.050		
	Mean[2]	62±10						71±76	3.6±3.8
March	1	100	1000	0.3686	0.3966	0.0284	0.030	30	1.5
	2	109	1000	0.3737	0.4462	0.0780	0.081	88	4.4
	3	106	1000	0.3684	0.3929	0.0247	0.026	28	1.4
	Mean[2]	105±5						49±34	2.4±1.7
May	1	143	1000	0.3895	0.5552	0.1870	0.195	279	14.0
	2	161	1000	0.3662	0.3687	0.0050	0.000	0	0.0
	3	183	1000	0.3658	0.3652	-0.0024	0.000	0	0.0
	Mean[2]	162±20						93±161	4.6±8.0

[1] Fertilizer N added at a rate of 2.28 μg N/g soil

[2] Means reported ± standard deviation.

APPENDIX B: Table 5. Experiment 1980B, Recovery of ^{15}N in NO_3-N fraction of a fallow Breton soil (0-13 cm).

Sampling date	Rep	x (μg)	y (μg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer recovery[1] (μg N/g)	Fertilizer recovery[1] (%)
November	1	199	3000	0.9570	9.870	9.501	9.88	0.98	42.8
	2	175	3000	1.1730	15.012	14.643	15.23	1.33	58.2
	3	182	3000	1.3993	18.435	18.066	18.79	1.71	74.7
	Mean[2]	185±12						1.34±0.36	58.6±15.9
January	1A	49	1000	0.4431	2.021	1.652	1.71	0.05	2.2
	1B	39	1000	0.4691	3.118	2.749	2.86		
	2A	133	1000	1.1292	6.869	6.500	6.76	0.38	16.8
	B	115	1000	0.9232	5.770	5.401	5.62		
	3A	52	1000	0.4579	2.229	1.860	1.93	0.05	2.3
	B	42	1000	0.4646	2.817	2.550	2.64		
	Mean[2]	72±41						0.16±0.19	7.1±8.4
March	1	159	1000	0.4530	1.064	0.695	0.72	0.06	2.5
	2	288	1000	1.3055	4.603	4.234	4.40	0.63	27.7
	3	218	1000	0.7161	2.369	2.000	2.08	0.23	10.0
	Mean[2]	222±65						0.31±0.29	20.9±9.5
May	1	1495	nil	N/A	0.9965	0.628	0.65	0.49	21.4
	2	1025	nil	N/A	1.3320	0.963	1.00	0.51	22.3
	3	825	nil	N/A	1.0134	0.644	0.67	0.28	12.2
	Mean[2]	1115±344						0.43±0.13	18.6±5.6

[1] Fertilizer N added at a rate of 2.29 μg N/g soil.
[2] Means reported ± standard deviation.

APPENDIX B: Table 6. Experiment 1980B, Recovery of ^{15}N in Total-N fraction of a fallow Breton soil (0-13 cm).

Sampling date	Rep	N in Sample (μ/g)	Excess (%)	Ndff (%)	Fertilizer Recovery[1] (μg N/g)	Fertilizer Recovery[1] (%)
November	1	2572	0.0706	0.073	1.15	50.2
	2	1591	0.0996	0.104	1.65	72.1
	3	1662	0.1268	0.132	2.19	95.6
	Mean[2]	1608±47			1.66±0.52	72.6±22.7
January	1	1560	0.0051	0.005	0.08	3.5
	2	1622	0.0456	0.047	0.76	33.2
	3	1684	0.0055	0.006	0.10	4.4
	Mean[2]	1622±62			0.31±0.39	13.7±16.9
March	1	1618	0.0059	0.006	0.10	4.4
	2	1606	0.0408	0.042	0.67	29.3
	3	1515	0.0171	0.018	0.27	11.8
	Mean[2]	1580±56			0.35±0.29	15.2±12.8
May	1	1442	0.0628	0.065	0.94	41.0
	2	1640	0.0377	0.039	0.64	27.9
	3	1675	0.0379	0.039	0.65	28.4
	Mean[2]	1586±126			0.74±0.17	32.3±7.4

[1] Fertilizer N added at a rate of 2.29 μg N/g soil.
[2] Means reported ± standard deviation.

APPENDIX B: Table 7. Experiment 1980B, Recovery of ^{15}N in NH_4-N fraction of a stubble Breton soil (0-13 cm).

Sampling date	Rep	x (μg)	y (μg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer recovery[1] (ng)	Fertilizer recovery[1] (ng N/g)
November	1A	63	1000	0.3724	0.4772	0.1090	0.113	60	3.0
	1B	74	1000	0.3704	0.4326	0.0644	0.067		
	2A	74	1000	0.3721	0.4572	0.0890	0.093	68	3.4
	2B	77	1000	0.3719	0.4511	0.0829	0.086		
	3A	101	1000	0.3778	0.4966	0.1284	0.134	95	4.8
	3B	88	1000	0.3708	0.4276	0.0594	0.062		
	Mean[2]	80±13						64±6	3.2±0.3
January	1A	64	1000	0.3760	0.5354	0.1672	0.174	116	5.8
	1B	64	1000	0.3769	0.5503	0.1821	0.189		
	2A	69	1000	0.3768	0.5362	0.1680	0.175	136	6.8
	2B	73	1000	0.3796	0.5686	0.2004	0.208		
	3A	65	1000	0.3720	0.4674	0.0992	0.103	88	4.4
	3B	57	1000	0.3742	0.5216	0.1534	0.160		
	Mean[2]	65±5						113±24	5.6±1.2
March	1	91	1000	0.3770	0.5000	0.1318	0.137	125	6.2
	2	112	1000	0.3892	0.5981	0.2299	0.239	268	13.4
	3	116	1000	0.3768	0.4716	0.1034	0.108	125	6.2
	Mean[2]	106±13						173±83	8.6±4.2
May	1	134	1000	0.3664	0.3708	0.0026	0.000	0	0.0
	2	133	1000	0.3661	0.3684	0.0002	0.000	0	0.0
	3	134	1000	0.3661	0.3683	0.0001	0.000	0	0.0
	Mean[3]	134±1						0	0.0

[1] Fertilizer N added at a rate of 2.32 μg N/g soil
[2] Means reported ± standard deviation.
[3] Not significantly different from natural abundance.

APPENDIX B: Table 8. Experiment 1980B, Recovery of ^{15}N in NO_3-N fraction of a stubble Breton soil (0-13 cm).

Sampling date	Rep	x (µg)	y (µg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer recovery[1] (µg N/g)	Fertilizer recovery[1] (%)
November	1A	57	3000	0.6542	15.833	15.464	16.08	0.43	18.5
	1B	58	1000	1.1109	13.961	13.592	14.14		
	2A	105	3000	0.8717	15.326	14.957	15.56	0.76	32.8
	2B	83	1000	1.6269	16.821	16.452	17.11		
	3A	76	3000	0.8634	20.506	20.137	20.95	0.73	31.5
	3B	64	1000	1.5606	20.229	19.860	20.66		
	Mean[2]	74±18						0.64±0.18	27.6±7.8
January	1A	47	1000	0.4973	3.295	1.926	2.91	0.08	3.5
	1B[3]	109	1000	0.6277	3.030	2.661	2.77		
	2	58	1000	0.6090	4.802	4.433	4.61	0.13	5.6
	3A	33	1000	0.5404	5.831	5.462	5.76	0.10	4.3
	3B	36	1000	0.5605	5.972	5.603	5.83		
	Mean[2]	46±11						0.10±0.03	4.3±1.3
March	1	174	1000	0.5053	1.307	0.938	0.98	0.08	3.5
	2	138	1000	0.5884	2.201	1.832	1.91	0.13	5.6
	3	146	1000	0.4040	0.666	0.197	0.31	0.02	0.9
	Mean[2]	153±20						0.08±0.05	3.4±2.2
May	1	1224	nil	N/A	0.876	0.507	0.527	0.32	13.8
	2	1160	nil	N/A	0.641	0.272	0.283	0.16	6.9
	3	1152	nil	N/A	0.660	0.291	0.303	0.17	7.3
	Mean[2]	1179±39						0.22±0.09	9.5±3.9

[1] Fertilizer N added at a rate of 2.32 µg N/g soil.
[2] Means reported ± standard deviation.
[3] Double aliquote distilled.

APPENDIX B: Table 9. Experiment 1980B, Recovery of ^{15}N in Total-N fraction of a stubble Breton soil (0-13 cm).

Sampling date	Rep	N in Sample (μ/g)	Excess (%)	Ndff (%)	Fertilizer Recovery[1] (μg N/g)	Fertilizer Recovery[1] (%)
November	1	1672	0.0468	0.049	0.82	35.3
	2	1678	0.0641	0.067	1.12	48.3
	3	1784	0.0782	0.081	1.44	62.1
	Mean[2]	1711±63			1.13±0.31	48.7±13.4
January	1	1718	0.0150	0.016	0.27	11.6
	2	1662	0.0216	0.022	0.36	15.5
	3	1663	0.0148	0.015	0.25	10.8
	Mean[2]	1681±32			0.29±0.06	12.5±2.5
March	1	1794	0.0171	0.018	0.32	13.8
	2	1700	0.223	0.023	0.39	16.8
	3	1555	0.0169	0.018	0.28	12.1
	Mean[2]	1682±79			0.33±0.06	14.2±2.6
May	1	1829	0.0222	0.023	0.42	18.1
	2	1573	0.0157	0.016	0.25	10.8
	3	1730	0.0142	0.015	0.26	11.2
	Mean[2]	1711±129			0.31±0.09	13.4±3.9

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[1] Fertilizer N added at a rate of 2.32 μg N/g soil.
[2] Means reported ± standard deviation.

APPENDIX B: Table 10. Experiment 1980B, Recovery of ^{15}N in NH_4-N fraction of a fallow Malmo soil (0-13 cm).

Sampling date	Rep	x (μg)	y (μg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer recovery[1] (ng)	Fertilizer recovery[1] (ng N/g)
November	1	130	1000	0.3739	0.4362	0.0690	0.072	94	4.7
	2	106	1000	0.3810	0.5244	0.1572	0.164	174	8.7
	3	132	1000	0.3816	0.5013	0.1341	0.139	183	9.2
	Mean[2]	123±14						150±49	7.5±2.4
January	1	138	1000	0.3718	0.4153	0.0481	0.050	69	3.4
	2	163	1000	0.3753	0.4336	0.0664	0.069	112	5.6
	3	93	1000	0.3723	0.4422	0.0750	0.0789	73	3.6
	Mean[2]	131±35						85±24	4.2±1.2
March	1	120	1000	0.3701	0.4059	0.0387	0.040	48	2.4
	2	120	1000	0.3781	0.4806	0.1134	0.118	142	7.1
	3	102	1000	0.3745	0.4598	0.0926	0.096	98	4.9
	Mean[2]	114±10						96±47	4.8±2.4
May	1	116	1000	0.3723	0.4283	0.0611	0.064	74	3.7
	2	120	1000	0.3737	0.4395	0.0723	0.075	90	4.5
	3	106	1000	0.3694	0.4034	0.0362	0.038	40	2.0
	Mean[2]	114±7						68±26	3.4±1.3

[1] Fertilizer N added at a rate of 2.41 μg N/g soil

[2] Means reported ± standard deviation.

APPENDIX B: Table 11. Experiment 1980B, Recovery of ^{15}N in NO_3-N fraction of a stubble Malmo soil (0-13 cm).

Sampling date	Rep	x (μg)	y (μg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer recovery[1] (μg N/g)	Fertilizer recovery[1] (%)
November	1	138	3000	0.9277	13.143	12.78	13.29	0.92	37.9
	2	108	3000	0.9482	17.126	16.76	17.43	0.94	38.9
	3	130	3000	0.9911	15.421	15.05	15.66	1.02	42.1
	Mean[2]	125±16						0.96±0.05	39.6±2.2
January	1	222	1000	1.0536	4.152	3.78	3.93	0.44	18.1
	2	263	1000	1.5182	5.900	5.53	5.75	0.64	26.4
	3	246	1000	1.5574	6.401	6.03	6.27	0.77	31.9
	Mean[2]	244±21						0.62±0.17	25.5±6.9
March	1	295[1]	1000	2.2317	8.557	8.19	8.52	1.26	52.1
	2	238	1000	1.6535	7.064	6.70	6.97	0.83	34.2
	3	277	1000	1.0906	8.317	7.95	8.27	1.14	47.3
	Mean[2]	270±29						1.08±0.22	44.5±9.3
May	1	464	1000	0.9965	2.356	1.99	2.07	0.48	19.8
	2	560	1000	1.3320	3.057	2.69	2.80	0.78	32.4
	3	522	1000	1.0134	2.254	1.89	1.97	0.51	21.2
	Mean[2]	515±48						0.59±0.18	24.5±6.9

[1] Fertilizer N added at a rate of 2.41 μg N/g soil.
[2] Means reported ± standard deviation.

APPENDIX B: Table 12. Experiment 1980B, Recovery of ^{15}N in Total-N fraction of a fallow Malmo soil (0-13 cm).

Sampling date	Rep	N in Sample (μ/g)	Excess (%)	Ndff (%)	Fertilizer Recovery[1] (μg N/g)	Fertilizer Recovery[1] (%)
November	1	4978	0.027	0.028	1.39	57.7
	2	4649	0.035	0.036	1.67	69.3
	3	4803	0.030	0.031	1.49	61.8
	Mean[2]	4810±165			1.52±0.14	63.1±5.8
January	1	4802	0.026	0.027	1.29	53.5
	2	4879	0.032	0.033	1.61	66.8
	3	5169	0.016	0.017	0.88	36.5
	Mean[2]	4950±194			1.26±0.36	52.3±14.9
March	1	5407	0.033	0.034	1.84	76.3
	2	5167	0.025	0.026	1.34	55.6
	3	5216	0.035	0.036	1.88	78.0
	Mean[2]	5263±127			1.69±0.30	70.1±12.4
May	1	4769	0.016	0.017	0.81	33.6
	2	5645	0.024	0.025	1.41	58.5
	3	5531	0.015	0.016	0.88	36.5
	Mean[2]	5315±476			1.03±0.33	42.7±13.7

[1] Fertilizer N added at a rate of 2.41 μg N/g soil.
[2] Means reported ± standard deviation.

APPENDIX B: Table 13. Experiment 1980B, Recovery of ^{15}N in NH_4-N fraction of a stubble Malmo soil (0-13 cm).

Sampling date	Rep	x (μg)	y (μg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer recovery[1] (ng)	Fertilizer recovery[1] (ng N/g)
November	1	123	1000	0.3724	0.4261	0.0589	0.061	75	3.8
	2	137	1000	0.3721	0.4181	0.0509	0.053	73	3.6
	3	145	1000	0.3778	0.4605	).933	0.097	141	7.0
	Mean[2]	135±11						96±39	4.8±2.0
January	1	106	1000	0.3762	0.4743	0.1071	0.111	118	5.9
	2	125	1000	0.3729	0.4297	0.0625	0.065	81	4.0
	3	120	1000	0.3731	0.4339	0.0667	0.069	83	4.2
	Mean[2]	117±10						94±21	4.7±1.0
March	1	125	1000	0.3703	0.4063	0.0391	0.041	51	2.6
	2	120	1000	0.3771	0.4713	0.1059	0.110	132	6.6
	3	127	1000	0.3753	0.4501	0.0829	0.086	109	5.4
	Mean[2]	124±4						97±42	4.8±2.1
May	1	153	1000	0.3804	0.4758	0.1086	0.113	173	8.6
	2	153	1000	0.3882	0.5346	0.1674	0.174	266	13.3
	3	144	1000	0.3781	0.4635	0.0963	0.100	144	7.2
	Mean[2]	150±5						194±64	9.7±3.2

[1] Fertilizer N added at a rate of 2.76 μg N/g soil.

[2] Means reported ± standard deviation.

APPENDIX B: Table 14. Experiment 1980B, Recovery of ^{15}N in NO$_3$-N fraction of a stubble Malmo soil (0-13 cm).

Sampling date	Rep	x (μg)	y (μg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer recovery[1] (μg N/g)	Fertilizer recovery[1] (%)
November	1	159	3000	0.9044	11.07	10.70	11.13	0.88	31.9
	2	218	3000	1.0021	9.76	9.39	9.77	1.06	38.4
	3	215	3000	1.3351	15.59	15.22	15.83	1.70	61.6
	Mean[2]	197±33						1.21±0.43	44.0±15.6
January	1A	263	1000	1.9173	7.82	7.45	7.75	1.01	36.6
	1B	251	1000	1.8940	7.98	7.61	7.92		
	2	194	1000	0.8549	3.38	3.01	3.13	0.30	10.8
	3	270	1000	1.0859	3.75	3.38	3.52	0.48	17.4
	Mean[2]	240±41						0.60±0.37	21.6±13.4
March	1	176	1000	1.0277	4.79	4.42	4.60	0.40	14.5
	2	369	1000	1.2020	3.47	3.10	3.22	0.59	21.4
	3	198	1000	1.1279	4.98	4.61	4.80	0.48	17.4
	Mean[2]	247±106						0.49±0.10	17.8±3.5
May	1A	67	1000	0.4037	0.97	0.60	0.62	0.02	0.8
	1B	74	1000	0.3992	0.85	0.48	0.50		
	2	127	1000	0.4768	1.35	0.98	1.01	0.06	2.2
	3A	35	1000	0.3812	0.82	0.45	0.47		
	3B	41	1000	0.3841	0.83	0.46	0.48	0.02	0.8
	Mean[2]	78±45						0.03±0.02	1.3±0.8

[1] Fertilizer N added at a rate of 2.76 μg N/g soil.
[2] Means reported ± standard deviation.

APPENDIX B: Table 15. Experiment 1980B, Recovery of ^{15}N in Total-N fraction of a stubble Malmo soil (0-13 cm).

Sampling date	Rep	N in Sample (µg/g)	Excess (%)	Ndff (%)	Fertilizer Recovery[1] (µg N/g)	Fertilizer Recovery[1] (%)
November	1	4911	0.0264	0.028	1.38	50.0
	2	5805	0.0255	0.027	1.57	56.9
	3	5766	0.0454	0.047	2.71	98.2
	Mean[2]	5562±434			1.89±0.72	68.4±26.1
January	1	5349	0.0332	0.035	1.87	67.8
	2	5677	0.0154	0.016	0.91	33.0
	3	5590	0.0150	0.016	0.89	32.2
	Mean[2]	5539±170			1.22±0.56	44.3±20.3
March	1	5153	0.0182	0.019	0.98	35.5
	2	5738	0.0262	0.027	1.55	56.1
	3	5580	0.0169	0.018	1.00	36.2
	Mean[2]	5490±303			1.18±0.32	42.6±11.7
May	1	4039	0.0084	0.009	0.36	13.0
	2	5687	0.0209	0.022	1.25	45.3
	3	5920	0.0159	0.017	1.00	36.2
	Mean[2]	5215±1025			0.87±0.46	31.5±16.7

[1] Fertilizer N added at a rate of 2.76 µg N/g soil.

[2] Means reported ± standard deviation.

APPENDIX B: Table 16. Experiment 1981A, Recovery of ^{15}N in the NH_4-N fraction of a Breton soil (0-15 cm).

Sampling date	Rep	x (μg)	y (μg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1]		
								ng	ng N/g	d ^{15}N
December	1	514	1000	0.3670	0.3693	0.0011	0.0011	6		3
	2	456	1000	0.3670	0.3696	0.0014	0.0015	7		4
	3	485	1000	0.3672	0.3700	0.0018	0.0019	9		5
	4	485	1000	0.3668	0.3689	0.0007	0.0007	3		2
	Mean[2]	485±24						6±2.5	0.13±0.6	4±1
January	1	358	1000	0.3680	0.3741	0.0059	0.0061	22		16
	2	272	1000	0.3681	0.3766	0.0084	0.0087	24		23
	3	358	1000	0.3688	0.3772	0.0090	0.0094	34		24
	4	262	1000	0.3690	0.3812	0.0130	0.0135	36		35
	Mean[2]	312±53						29±7	0.64±0.15	24±8
March	1	561	1000	0.3673	0.3700	0.0018	0.0019	11		5
	2	431	1000	0.3673	0.3708	0.0026	0.0027	12		7
	3	439	1000	0.3676	0.3717	0.0035	0.0036	16		10
	4	446	1000	0.3672	0.3703	0.0021	0.0022	10		6
	Mean[2]	469±61						12±3	0.27±0.07	7±2
May	1	164	1000	0.3683	0.3835	0.0153	0.0159	26		42
	2	125	1000	0.3665	0.3721	0.0039	0.0041	5		11
	3	138	1000	0.3673	0.3782	0.0100	0.0104	14		27
	4	125	1000	0.3669	0.3757	0.0075	0.0078	10		20
	Mean[2]	138±18						14±9	0.31±0.20	25±13

[1] Fertilizer N added as KNO_3 in the fall of the previous year (October 1980) at a rate of 2.32 μg N/g soil.
[2] Means reported ± standard deviation.

APPENDIX B: Table 17. Experiment 1981A, Recovery of ^{15}N in the NO_3-N fraction of a Breton soil (0-15 cm).

Sampling date	Rep	x (µg)	y (µg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1]		
								ng	ng N/g	d-^{15}N
December	1A	160	500	0.3799	0.4208	0.0518	0.054	88		139
	1B	171	1000	0.3736	0.4198	0.0508	0.053			
	2	122	1000	0.3705	0.4090	0.0400	0.042	51		108
	3	152	1000	0.3725	0.4291	0.0601	0.063	96		163
	4	153	1000	0.3756	0.4351	0.0661	0.069	106		179
	Mean[2]	152±18						85±24	1.89±0.53	147±31
January	1	163	1000	0.3817	0.4792	0.1102	0.115	187		299
	2	166	1000	0.3774	0.4473	0.0783	0.081	134		212
	3	144	1000	0.3791	0.4715	0.1025	0.117	168		277
	4	127	1000	0.3830	0.5184	0.1494	0.155	197		405
	Mean[2]	150±18						172±28	3.81±0.62	298±80
March	1	178	1000	0.3743	0.4220	0.0530	0.055	98		144
	2	217	1000	0.3737	0.4101	0.0411	0.043	93		111
	3	192	1000	0.3743	0.4186	0.0496	0.052	100		134
	4	181	1000	0.3739	0.4186	0.0496	0.052	94		134
	Mean[2]	192±18						96±3	2.13±0.07	131±14
May	1	88	1000	0.3697	0.4140	0.0450	0.047	41		122
	2	105	1000	0.3689	0.3984	0.0294	0.031	33		80
	3	104	1000	0.3715	0.4263	0.0573	0.060	62		155
	4	110	1000	0.3684	0.3920	0.0230	0.024	26		62
	Mean[2]	102±10						40±16	0.88±0.36	105±42

[1] Fertilizer N added as KNO_3 in the fall of the previous year (October 1980) at a rate of 2.32 µg N/g soil.
[2] Means reported ± standard deviation.

APPENDIX B: Table 18. Experiment 1981A, Recovery of ^{15}N in the Organic-N fraction of a Breton soil (0-15 cm).

Sampling date	Rep	μg N g soil	At Ab (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1]	
						ng/g	d ^{15}N
December	1	1472	0.3720	0.0040	0.0046	68	12
	2	1542	0.3721	0.0045	0.0047	72	12
	3	1383	0.3716	0.0040	0.0042	58	11
	4	1504	0.3718	0.0042	0.0044	66	11
	Mean[2]	1475±68				66±6	12±1
January	1	1477	0.3717	0.0041	0.0043	64	11
	2	1601	0.3718	0.0042	0.0044	70	11
	3	1452	0.3717	0.0041	0.0043	62	11
	4	1425	0.3719	0.0043	0.0045	64	12
	Mean[2]	1489±78				65±3	11±1
March	1	1492	0.3721	0.0045	0.0047	70	12
	2	1596	0.3721	0.0045	0.0047	75	12
	3	1339	0.3718	0.0042	0.0044	59	11
	4	1535	0.3720	0.0044	0.0046	71	12
	Mean[2]	1490±110				69±7	12±1
May	1	1503	0.3712	0.0036	0.0037	56	10
	2	1622	0.3703	0.0027	0.0008	45	7
	3	1427	0.3712	0.0036	0.0037	53	10
	4	1556	0.3709	0.0033	0.0034	53	9
	Mean[2]	1527±83				52±5	9±1

[1] Fertilizer N added as KNO, in the fall of the previous year (October 1980) at a rate of 2.32 μg N/g soil.

[2] Means reported ± standard deviation.

APPENDIX B: Table 19. Experiment 1981A, Recovery of ^{15}N in the NH_4-N fraction of a Malmo soil (0-15 cm).

Sampling date	Rep	x (μg)	y (μg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1]		
								ng	ng N/g	d ^{15}N
December	1	446	1000	0.3709	0.3823	0.0151	0.016	71		41
	2	585	1000	0.3701	0.3744	0.0102	0.011	64		28
	3	479	1000	0.3709	0.3815	0.0143	0.015	72		39
	4	578	1000	0.3706	0.3789	0.0117	0.012	69		32
	Mean[2]	522±70						69±4	1.53±0.09	35±6
January	1	305	1000	0.3726	0.3949	0.0277	0.029	88		75
	2	326	1000	0.3725	0.3930	0.0258	0.027	88		70
	3	301	1000	0.3715	0.3904	0.0232	0.024	62		63
	4	233	1000	0.3701	0.3885	0.0213	0.022	51		58
	Mean[2]	291±40						72±12	1.60±0.27	66±8
March	1	479	1000	0.3704	0.3800	0.0128	0.013	62		35
	2	542	1000	0.3725	0.3849	0.0177	0.018	97		48
	3	540	1000	0.3703	0.3786	0.0114	0.012	65		31
	4	645	1000	0.3720	0.3816	0.0144	0.015	97		39
	Mean[2]	552±69						80±19	1.78±0.42	38±7
May	1	186	1000	0.3702	0.3938	0.0266	0.028	52		72
	2	158	1000	0.3698	0.3951	0.0279	0.029	46		76
	3	162	1000	0.3698	0.3945	0.0273	0.028	45		74
	4	246	2000	0.3681	0.3868	0.0196	0.020	49		53
	Mean[2]	188±41						48±3	1.07±0.007	69±11

[1] Fertilizer N added as KNO_3 in the fall of the previous year (October 1980) at a rate of 2.41 μg N/g soil.
[2] Means reported ± standard deviation.

APPENDIX B: Table 20. Experiment 1981A, Recovery of ^{15}N in the NO$_3$-N fraction of a Malmo soil (0-15 cm).

Sampling date	Rep	x (μg)	y (μg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1]		
								ng	ng N/g	d ^{15}N
December	1	290	1000	0.3987	0.5121	0.1443	0.150	435		392
	2	321	1000	0.4003	0.5078	0.1400	0.146	469		381
	3	316	1000	0.4018	0.5157	0.1479	0.154	486		402
	4	312	1000	0.4000	0.5096	0.1418	0.148	462		386
	Mean[2]	310±14						463±21	10.29±0.47	390±9
January	1	220	1000	0.4143	0.6348	0.2670	0.278	612		726
	2	359	1000	0.4128	0.5494	0.1816	0.189	679		494
	3	342	1000	0.4142	0.5557	0.1879	0.195	667		511
	4	301	1000	0.4044	0.5326	0.1648	0.171	515		448
	Mean[2]	306±62						618±75	13.73±1.67	545±124
March	1	374	1000	0.3982	0.4848	0.1170	0.122	456		318
	2	326	1000	0.4046	0.5236	0.1558	0.162	528		423
	3	316	1000	0.4013	0.5136	0.1458	0.152	480		396
	4	361	1000	0.4012	0.4993	0.1315	0.137	495		358
	Mean[2]	344±28						490±30	10.89±0.67	374±46
May	1	436	1000	0.4137	0.5237	0.1559	0.162	706		423
	2	203	1000	0.3877	0.4956	0.1278	0.134	272		347
	3	216	1000	0.3895	0.4992	0.1314	0.137	296		357
	4	135	1000	0.3819	0.5012	0.1334	0.139	188		363
	Mean[2]	248±130						365±231	8.11±5.11	372±34

[1] Fertilizer N added as KNO$_3$ in the fall of the previous year (October 1980) at a rate of 2.41 μg N/g soil.
[2] Means reported ± standard deviation.

APPENDIX B: Table 21. Experiment 1981A, Recovery of ^{15}N in the Organic-N fraction of a Malmo soil (0-15 cm).

Sampling date	Rep	μg N g soil	At Ab (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1]	
						ng/g	d ^{15}N
December	1	4481	0.3801	0.0129	0.0134	600	35
	2	4657	0.3810	0.0138	0.0144	671	38
	3	4769	0.3798	0.0126	0.0131	625	34
	4	4682	0.3800	0.0128	0.0133	623	35
	Mean[2]	4647±121				630±30	36±2
January	1	4853	0.3786	0.0114	0.0119	578	31
	2	4752	0.3795	0.0123	0.0128	621	33
	3	4615	0.3789	0.0117	0.0122	563	31
	4	4549	0.3795	0.0123	0.0128	582	33
	Mean[2]	4692±137				586±25	32±1
March	1	4573	0.3770	0.0098	0.0102	466	27
	2	4692	0.3781	0.0109	0.0113	530	30
	3	4614	0.3753	0.0081	0.0084	388	22
	4	4601	0.3793	0.0121	0.0126	580	33
	Mean[2]	4620±51				491±83	28±5
May	1	4858	0.3784	0.0112	0.0117	568	30
	2	4732	0.3779	0.0[illegible]07	0.0111	525	29
	3	4718	0.3780	0.0108	0.0112	528	29
	4	4836	0.3758	0.0086	0.0089	430	23
	Mean[2]	4786±71				513±59	28±3

[1] Fertilizer N added as KNO_3 in the fall of the previous year (October 1980) at a rate of 2.41 μg N/g soil.
[2] Means reported ± standard deviation.

APPENDIX B: Table 22. Experiment 1981B, Recovery of ^{15}N in NH_4-N fraction of a residue amended Breton soil (0-15 cm).

Sampling date	Rep	x (μg)	y (μg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1]	
								(ng)	(ng N/g)
December	1	478	1000	0.4968	0.7709	0.403	0.419	2003[3]	44[3]
	2	458	1000	0.5163	0.8449	0.477	0.496	2272	50
	3	473	1000	0.5182	0.8404	0.472	0.491	2322	52
	4	466	1000	0.5000	0.7880	0.420	0.437	2036	45
	Mean[2]	469±9						2180±147	49±4
January	1	315	1000	0.4401	0.6760	0.308	0.320	1008	22
	2	315	1000	0.4336	0.6488	0.281	0.292	920	20
	3	344	1000	0.4419	0.6631	0.295	0.307	1056	23
	4	372	1000	0.4194	0.5635	0.195	0.203	755	17
	Mean[2]	336±27						935±132	20±3
March	1	444	1000	0.4427	0.6159	0.248	0.258	1146	25
	2	410	1000	0.4361	0.6076	0.239	0.249	1021	23
	3	485	1000	0.4339	0.5743	0.206	0.214	1038	23
	4	433	1000	0.4242	0.5591	0.191	0.199	862	19
	Mean[2]	443±31						1017±117	22±3
May	1	259	1000	0.4038	0.5505	0.182	0.189	490	11
	2	228	1000	0.3965	0.5311	0.163	0.170	388	9
	3	280	1000	0.3807	0.4339	0.066	0.069	193	4
	4	220	1000	0.4000	0.555	0.187	0.194	427	9
	Mean[2]	247±28						374±128	8±3

[1] Fertilizer N added November 1981 at a rate of 5.21 μg N/g soil.
[2] Means reported ± standard deviation.
[3] Deleted from calculation of the mean and ANOVA.

APPENDIX B: Table 23. Experiment 1981B, Recovery of ^{15}N in NO_3-N fraction of a residue amended Breton soil (0-15 cm).

Sampling date	Rep	x (µg)	y (µg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1] (µg N/g)	Fertilizer Recovery[1] (%)
December	1	186	10000	0.8435	26.53	26.16	27.21	1.12[4]	21.5[4]
	2	195	10000	0.8475	25.55	25.18	26.19	1.13	21.7
	3	220	10000	1.0399	31.68	31.31	32.57	1.59	30.5
	4	200	10000	0.8018	22.60	22.23	23.12	1.03	19.8
	Mean[2]	200±24						1.25±0.30	24.0±5.7
January	1	231	10000	1.1006	32.91	32.54	33.85	1.74	33.4
	2	179	10000	0.9455	33.33	32.96	34.29	1.36	26.1
	3	227	10000	1.0706	32.36	31.99	33.28	1.68	32.2
	4	242	10000	1.0807	30.62	30.25	31.47	1.69	32.4
	Mean[2]	220±28						1.62±0.17	31.0±3.3
March	1	192	10000	0.8335	25.19	24.82	25.82	1.10	21.1
	2	151	10000	0.7750	27.87	27.50	28.61	0.96	18.4
	3	217	10000	0.7088	16.52	16.15	16.80	0.81	15.5
	4	176	10000	0.8430	27.96	27.59	28.70	1.12	21.5
	Mean[2]	184±28						100±0.14	19.1±2.8
May	1A	31	2000	0.3882	1.833	1.46	1.52	0.01	0.2
	1B[3]	102	1000	0.5283	2.121	1.75	1.82	0.01	0.2
	2A	31	2000	0.3968	2.397	2.03	2.11		
	2B[3]	94	1000	0.5018	1.949	1.58	1.64	0.01	0.2
	3A	48	2000	0.3804	0.989	0.62	0.65		
	3B[3]	131	1000	0.5134	1.560	1.19	1.24	0.02	0.4
	4A	49	2000	0.4000	1.796	1.43	1.49		
	4B[3]	162	1000	0.6148	2.152	1.78	1.85		
	Mean[2]	40±10						0.01±0.01	0.2±0.1

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[1] Fertilizer N added November 1981 at a rate of 5.21 µg N/g soil.

[2] Means reported ± standard deviation.

[3] Triple aliquote distilled.

[4] Deleted from calculation of the mean and from ANOVA.

APPENDIX B: Table 24. Experiment 1981B, Recovery of ^{15}N in the Organic-N fraction of a residue amended Breton soil (0-15 cm).

Sampling date	Rep	μg N g soil	At Ab (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1] μg N/g	Fertilizer Recovery[1] (%)
December	1A	1605	0.8043	0.4367	0.454	7.29[3]	139.9[3]
	1B	1622	0.8051	0.4375	0.455	7.38[3]	141.7[3]
	2	1586	0.5667	0.1991	0.207	3.28	62.9
	3	1639	0.6079	0.2403	0.250	4.10	78.7
	4	1619	0.6727	0.3051	0.317	5.13	98.5
	Mean[2]	1614±22				4.17±0.93	80.0±17.8
January	1	1630	0.5472	0.1796	0.187	3.05	58.5
	2	1513	0.4615	0.0939	0.098	1.48	28.4
	3	1658	0.4678	0.1002	0.104	1.72	33.0
	4	1602	0.4880	0.1204	0.125	2.00	38.4
	Mean[2]	1601±63				2.06±0.69	39.5±43.2
March	1	1633	0.4203	0.0527	0.055	0.90	17.3
	2	1563	0.4371	0.0695	0.072	1.12	21.5
	3	1654	0.4408	0.0732	0.076	1.26	22.2
	4	1607	0.4258	0.0582	0.061	0.98	18.8
	Mean[2]	1614±39				1.06±0.16	20.0±2.4
May	1	1626	0.4571	0.0895	0.093	1.51	29.0
	2	1658	0.4828	0.1152	0.120	1.99	38.2
	3	1556	0.4811	0.1135	0.118	1.83	35.1
	4	1624	0.4779	0.1103	0.114	1.86	35.7
	Mean[2]	1616±43				1.80±0.20	34.5±3.9

[1] Fertilizer N added November 1981 at a rate of 5.21 μg N/g soil.
[2] Means reported ± standard deviation.
[3] Deleted from calculation of the mean and from ANOVA.

APPENDIX B: Table 25. Experiment 1981B, Recovery of ^{15}N in NH_4-N fraction of a non-amended Breton soil (0-15 cm).

Sampling date	Rep	x (μg)	y (μg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1] (ng)	Fertilizer Recovery[1] (ng N/g)
December	1	524	1000	0.4149	0.5086	0.1404	0.146	765	17
	2	528	1000	0.4030	0.4734	0.1052	0.109	576	13
	3	533	1000	0.4070	0.4843	0.1161	0.121	645	14
	4	441	1000	0.4149	0.5261	0.1579	0.164	723	16
	Mean[2]	506±44						677±84	15±2
January	1	303	1000	0.3886	0.4638	0.0956	0.099	299	7
	2	384	1000	0.3959	0.4743	0.1061	0.114	438	10
	3	353	1000	0.3975	0.4873	0.1191	0.124	438	10
	4	317	1000	0.3864	0.4514	0.0832	0.087	276	6
	Mean[2]	339±37						363±87	8±2
March	1	454	1000	0.3815	0.4162	0.0480	0.050	227	5
	2	550	1000	0.3791	0.4033	0.0351	0.037	203	5
	3	528	1000	0.3788	0.4034	0.0352	0.037	195	4
	4	500	1000	0.3835	0.4189	0.0507	0.053	265	6
	Mean[2]	508±41						225±31	5±1
May	1	141	1000	0.3736	0.4289	0.0607	0.063	89	2
	2	139	1000	0.3709	0.4076	0.0394	0.041	57	1
	3	155	1000	0.3729	0.4187	0.0505	0.052	81	2
	4	150	1000	0.3792	0.4685	0.1003	0.104	156	4
	Mean[2]	146±8						96±42	2±1

[1] Fertilizer N added November 1981 at a rate of 5.21 μg N/g soil.

[2] Means reported ± standard deviation.

APPENDIX B: Table 26. Experiment 1981B, Recovery of ^{15}N in NO$_3$-N fraction of a residue non-amended Breton soil (0-15 cm).

Sampling date	Rep	x (μg)	y (μg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1] (μg N/g)	Fertilizer Recovery[1] (%)
December	1	252	10000	1.2294	35.50	36.13	37.58	2.10	40.3
	2	311	10000	1.4594	36.62	36.25	37.71	2.61	50.1
	3	178	10000	1.0006	36.66	36.29	37.75	1.49	28.6
	4	232	10000	1.2012	33.63	33.26	34.60	1.78	34.2
	Mean[2]	243±55						2.00±0.48	38.4±9.2
January	1	220	10000	1.4594	51.17	50.80	52.84	2.58	49.5
	2	263	10000	1.2370	34.36	33.99	35.36	2.07	39.7
	3	202	10000	1.0743	36.15	35.78	37.22	1.67	32.1
	4	199	10000	1.0377	34.80	34.43	35.82	1.58	30.3
	Mean[2]	221±29						1.98±0.46	37.9±8.7
March	1	285	5000	1.8703	28.27	27.90	29.02	1.84	35.3
	2	248	5000	1.4516	23.34	22.97	23.89	1.32	25.3
	3	335	5000	1.9660	25.85	25.48	26.51	1.97	37.8
	4	298	5000	2.0213	29.80	29.43	30.61	2.03	39.0
	Mean[2]	292±36						1.79±0.32	34.4±6.2
May	1A	78	5000	0.3921	2.08	1.71	1.78	0.04	0.8
	1B[3]	150	1000	0.6603	2.62	2.25	2.34		
	2A	76	5000	0.3837	1.56	1.19	1.24	0.02	0.4
	2B[3]	141	1000	0.5444	1.81	1.44	1.50		
	3	136	5000	0.3899	1.28	0.91	0.95	0.03	0.6
	4	123	5000	0.4508	3.91	3.54	3.68	0.10	1.9
	Mean[2]	93±28						0.05±0.04	1.0±0.8

[1] Fertilizer N added November 1981 at a rate of 5.21 μg N/g soil.
[2] Means reported ± standard deviation.
[3] Double aliquote distilled.

APPENDIX B: Table 27. Experiment 1981A, Recovery of ^{15}N in the Organic-N fraction of a non-amended Breton soil (0-15 cm).

Sampling date	Rep	µg N g soil	At Ab (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1] (µg/g)	Fertilizer Recovery[1] (%)
December	1	1443	0.3990	0.0314	0.033	0.48	9.2
	2	1518	0.3956	0.0280	0.029	0.44	8.4
	3	1402	0.3936	0.0260	0.027	0.38	7.3
	4	1476	0.4018	0.0342	0.036	0.53	10.2
	Mean[2]	1460±49				0.46±0.06	8.8±1.2
January	1	1547	0.3788	0.0112	0.012	0.19	3.6
	2	1582	0.3794	0.0118	0.012	0.19	3.6
	3	1488	0.3781	0.0105	0.011	0.16	3.1
	4	1565	0.4262	0.0586	0.061	0.39	7.5
	Mean[2]	2546±41				0.23±0.11	4.4±2.1
March	1	1596	0.3788	0.0112	0.012	0.19	3.6
	2	1528	0.3778	0.0102	0.011	0.17	3.3
	3	1594	0.3788	0.0112	0.012	0.19	3.6
	4	1312	0.4105	0.0429	0.045	0.59	11.3
	Mean[2]	1508±134				0.28±0.20	5.4±3.8
May	1	1547	0.3766	0.0090	0.009	0.14	2.7
	2	1538	0.3749	0.0073	0.008	0.12	2.3
	3	1505	0.3741	0.0065	0.007	0.11	2.1
	4	1536	0.3829	0.0153	0.016	0.25	4.8
	Mean[2]	1532±18				0.16±0.06	3.0±1.2

[1] Fertilizer N added November 1981 at a rate of 5.21 µg N/g soil.

[2] Means reported ± standard deviation.

APPENDIX B: Table 28. Experiment 1981B, Recovery of ^{15}N in NH$_4$-N fraction of a residue amended Malmo soil (0-15 cm).

Sampling date	Rep	x (μg)	y (μg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1] (ng)	Fertilizer Recovery[1] (ng N/g)
December	1	475	1000	0.4048	0.4869	0.1197	0.124	589	13
	2	439	1000	0.4062	0.4982	0.1310	0.136	597	13
	3	490	1000	0.4172	0.5221	0.1549	0.161	789	18
	4	514	1000	0.4052	0.4819	0.1147	0.119	612	14
	Mean[2]	480±31						647±95	14±2
January	1	393	1000	0.3810	0.4197	0.0525	0.055	216	5
	2	387	1000	0.3783	0.4106	0.0434	0.045	174	4
	3	329	1000	0.3781	0.4155	0.483	0.050	164	4
	4	355	1000	0.3927	0.4685	0.1013	373	8	
	Mean[2]	366±30						232±97	5±2
March	1	569	1000	0.3927	0.4400	0.0728	0.076	432	10
	2	576	1000	0.3991	0.4569	0.897	0.093	536	12
	3	552	1000	0.4139	0.5010	0.1338	0.139	767	17
	4	634	1000	0.3919	0.4331	0.0659	0.069	437	10
	Mean[2]	583±36						543±157	12±3
May	1	228	1000	0.4496	0.8171	0.4499	0.468	1067	24
	2	248	1000	0.3895	0.5354	0.1682	0.175	434	10
	3	228	1000	0.4675	0.9136	0.5464	0.568	1295	29
	4	374	1000	0.3891	0.4514	0.0842	0.088	329	7
	Mean[2]	270±70						781±473	18±11

[1] Fertilizer N added November 1981 at a rate of 5.78 μg N/g soil.
[2] Means reported ± standard deviation.

APPENDIX B: Table 29. Experiment 1981B, Recovery of ^{15}N in NO_3-N fraction of a residue amended Malmo soil (0-15 cm).

Sampling date	Rep	x (μg)	y (μg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1] (μg/g)	Fertilizer Recovery[1] (%)
December	1	224	20000	0.5948	21.04	20.67	21.50	1.07	18.5
	2	166	20000	0.5130	18.25	17.88	18.60	0.69	11.9
	3	192	20000	0.5655	21.37	21.00	21.84	0.93	16.1
	4	194	20000	0.5830	22.97	22.60	23.51	1.01	17.5
	Mean[2]	194±24						0.92±0.17	15.9±2.9
January	1	233	20000	0.6141	21.93	21.56	22.43	1.16	20.1
	2	244	20000	0.5847	18.53	18.16	18.89	1.02	17.6
	3	162	20000	0.5216	19.76	19.39	20.17	0.73	12.6
	4	228	20000	0.5910	20.34	19.97	20.77	1.05	18.2
	Mean[2]	217±37						0.99±0.18	17.1±3.2
March	1	227	10000	0.7241	16.51	16.14	17.07	0.96 T14.9	
	2	279	10000	0.7319	13.85	13.48	14.02	0.87	15.0
	3	199	10000	o.6047	12.61	12.24	12.73	0.56	9.7
	4	237	10000	0.7597	17.38	17.01	17.69	0.93	16.1
	Mean[2]	236±33						0.80±0.17	13.8±2.9
May	1	206	10000	0.5545	9.71	9.34	9.72	0.44	7.6
	2A	65	10000	0.3815	2.80	2.43	2.53	0.04	1.0
	2B[3]	143	1000	0.8602	4.32	3.95	4.11	0.07	
	3	162	10000	0.5492	11.87	11.50	11.96	0.43	7.4
	4A	109	10000	0.3751	1.23	0.86	0.89	0.02	0.5
	4B[3]	213	1000	0.6764	2.13	1.76	1.83	0.04	
	Mean[2]	136±60						0.24±0.23	4.2±4.0

[1] Fertilizer N added at a rate of 5.78 μg N/g soil.
[2] Means reported ± standard deviation.
[3] Double aliquote distilled.

APPENDIX B: Table 30. Experiment 1981B, Recovery of ^{15}N in the Organic-N fraction of a residue amended Malmo soil (0-15 cm).

Sampling date	Rep	µg N g soil	At Ab (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1]	
						(µg/g)	(%)
December	1	4776	0.3902	0.0230	0.024	1.14	19.7
	2	4496	0.3902	0.0230	0.024	1.07	18.5
	3	4800	0.3937	0.0265	0.028	1.34	23.2
	4	4679	0.3923	0.0251	0.026	1.22	21.1
	Mean[2]	4688±138				1.19±0.12	20.6±2.0
January	1	4892	0.3734	0.0062	0.006	0.29	5.0
	2	4809	0.3748	0.0076	0.008	0.38	6.6
	3	4834	0.3781	0.0109	0.011	0.53	9.2
	4	4803	0.3732	0.0060	0.006	0.29	5.0
	Mean[2]	4834±41				0.37±0.11	6.4±1.9
March	1	4818	0.3765	0.0093	0.010	0.48	8.3
	2	4657	0.3806	0.0134	0.014	0.65	11.2
	3	4901	0.3782	0.0110	0.011	0.54	9.3
	4	4531	0.3772	0.0100	0.010	0.45	7.8
	Mean[2]	4727±165				0.45±0.13	7.8±2.2
May	1	4869	0.3975	0.0303	0.032	1.56	27.0
	2	4791	0.3757	0.0085	0.009	0.43	7.4
	3	4941	0.3925	0.0253	0.026	1.28	22.1
	4	4552	0.3725	0.0053	0.006	0.27	4.7
	Mean[2]	4788±169				0.88±0.63	15.2±10.9

[1] Fertilizer N added at a rate of 5.78 µg N/g soil.

[2] Means reported ± standard deviation.

APPENDIX B: Table 31. Experiment 1981B, Recovery of ^{15}N in NH_4-N fraction of non-amended Malmo soil (0-15 cm).

Sampling date	Rep	x (μg)	y (μg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1] (ng)	(ng N/g)
December	1	514	1000	0.4061	0.4845	0.1173	0.122	626	14
	2	482	1000	0.3904	0.4414	0.0742	0.077	369	8
	3	533	1000	0.3910	0.4383	0.0711	0.074	396	9
	4	585	1000	0.3942	0.4427	0.0755	0.079	464	10
	Mean[2]	528±43						464±117	10±3
January	1	294	1000	0.3731	0.3979	0.0307	0.032	94	2
	2	272	1000	0.3963	0.5084	0.1412	0.147	400	9
	3	276	1000	0.3760	0.4129	0.0457	0.048	266	6
	4	360	1000	0.3760	0.4043	0.0371	0.039	140	3
	Mean[2]	300±41						225±140	5±3
March	1	527	1000	0.3811	0.4101	0.429	0.045	234	5
	2	472	1000	0.3764	0.3986	0.0314	0.033	153	3
	3	506	1000	0.3815	0.4125	0.0453	0.047	238	5
	4	566	1000	0.3810	0.4079	0.0407	0.042	238	5
	Mean[2]	518±39						216±40	5±1
May	1	163	1000	0.3699	0.3950	0.0278	0.029	50	1
	2	175	1000	0.3861	0.5021	0.1349	0.140	243	5
	3	136	1000	0.3737	0.4318	0.0646	0.067	90	2
	4	137	1000	0.3709	0.4081	0.0346	0.036	50	1
	Mean[2]	153±19						108±90	2±2

[1] Fertilizer N added at a rate of 5.78 μg N/g soil.

[2] Means reported ± standard deviation.

APPENDIX B: Table 32. Experiment 1981B, Recovery of ^{15}N in NO_3-N fraction of a non-amended Malmo soil (0-15 cm).

Sampling date	Rep	x (µg)	y (µg)	Am (%)	Ao (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1] (µg N/g)	Fertilizer Recovery[1] (%)
December	1	470	20000	0.9509	25.85	25.48	26.51	2.77	47.9
	2	430	20000	0.9400	27.65	27.28	28.38	2.71	46.9
	3	449	20000	0.9984	29.18	28.81	29.97	2.99	51.7
	4	408	20000	0.8495	24.56	24.19	25.16	2.28	39.4
	Mean[2]	439±26						2.69±0.30	[illegible].5±5.2
January	1	368	20000	0.7631	22.36	21.99	22.87	1.87	32.4
	2	500	20000	0.8601	20.63	20.26	21.08	2.34	40.5
	3	426	20000	0.8643	24.27	23.90	24.86	2.35	40.7
	4	501	20000	0.9587	24.63	24.26	25.24	2.81	48.6
	Mean[2]	448±64						2.34±0.38	40.5±6.6
March	1	351	10000	1.2170	25.47	25.10	26.11	2.03	35.1
	2	393	10000	1.0211	17.70	17.33	18.03	1.57	27.2
	3	465	10000	1.2577	20.44	20.07	20.89	2.16	37.4
	4	372	10000	1.0343	19.00	18.63	19.38	1.60	27.7
	Mean[2]	395±50						1.84±0.30	31.8±5.2
May	1	125	10000	0.4003	3.16	2.79	2.90	0.08	1.4
	2	318	5000	0.6435	5.01	4.64	4.83	0.34	5.9
	3	223	5000	0.7274	8.84	8.47	8.81	0.44	7.6
	4	161	5000	0.4925	4.43	4.06	4.22	0.15	2.6
	Mean[2]	207±84				5.78.		0.25±0.17	4.3±2.9

[1] Fertilizer N added at a rate of 5.78 µg N/g soil.
[2] Means reported ± standard deviation.

APPENDIX B: Table 33. Experiment 1981B, Recovery of ^{15}N in the Organic-N fraction of a non-amended Malmo soil (0-15 cm).

Sampling date	Rep	μg N g soil	At Ab (%)	Excess (%)	Ndff (%)	Fertilizer Recovery[1] (μg/g)	Fertilizer Recovery[1] (%)
December	1	5048	0.3725	0.0053	0.006	0.30	5.2
	2	4933	0.3737	0.0065	0.007	0.35	6.0
	3	4889	0.3751	0.0079	0.008	0.39	6.7
	4	4939	0.3770	0.0098	0.010	0.49	8.5
	Mean[2]	4952±68				0.38±0.08	6.6±1.4
January	1	4956	0.3700	0.0028	0.003	0.15	2.6
	2	4816	0.3693	0.0021	0.002	0.09	1.7
	3	4796	0.3704	0.0032	0.003	0.14	2.4
	4	4786	0.3696	0.0024	0.002	0.10	1.7
	Mean[2]	4838±79				0.12±0.03	2.1±0.5
March	1	4833	0.3707	0.0035	0.004	0.19	3.3
	2	4849	0.3711	0.0039	0.004	0.19	3.3
	3	4802	0.3711	0.0039	0.004	0.19	3.3
	4	5072	0.3711	0.0039	0.004	0.20	3.5
	Mean[2]	4889±124				0.19±0.01	3.4±0.1
May	1	4610	0.3700	0.0028	0.003	0.14	2.4
	2	4707	0.3726	0.0054	0.006	0.28	4.8
	3	4511	0.3712	0.0040	0.004	0.18	3.1
	4	4633	0.3703	0.0031	0.003	0.14	2.4
	Mean[2]	4615±81				0.18±0.07	3.1±1.2

[1] Fertilizer N added at a rate of 5.78 μg N/g soil.
[2] Means reported ± standard deviation.

APPENDIX C

Miscellaneous Data Tables

APPENDIX C: Table 1. Recovery of NH_4-N and NO_3-N by steam distillation from 20 ml of solution containing 10μg/ml of NH_4-N and 10 μg/ml of NO_3-N[1]

	Recovery of N			
	NH_4-N		NO_3-N	
Rep	(μg-N)	%	(μg-N)	(%)
1	204	102	209	105
2	212	106	197	98
3	211	105	210	105
4	211	106	209	105
5	216	108	211	106
6	204	102	212	106
7	209	105	211	106
8	211	106	211	106
8	211	106	211	106
10	209	105	209	104
Mean ± std.dev.	210±4	105±2	208±5	104±2

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[1] Standards run with determination of NH_4-N and NO_3-N contents for Experiments 1980B, 1981A, 1981B.

APPENDIX C: Table 2. Bulk densities of soils used in Experiment 1980A.

Soil series	Treatment	Rep No.	Depth (cm)	Db (g/cm^3)	Depth (cm)	Db (g/cm^3)	Depth (cm)	Db (g/cm^3)
Breton	fallow	1	0-15	1.02	15-30	1.51	30-60	1.63
		2		1.05		1.41		1.48
		3		1.01		1.50		1.58
		Mean[1]		1.03±0.02		1.47±0.06		1.56±0.08
Didsbury	fallow	1	0-15	1.00	15-30	1.39	30-60	1.6
		2		1.05		1.36		1.68
		3		0.87		1.26		1.62
		Mean[1]		0.97±0.09		1.34±0.07		1.64±0.03
Didsbury	stubble	1	0-15	1.00	15-30	1.40	30-60	1.75
		2		1.31		1.34		1.53
		3		1.24		1.35		1.58
		Mean[1]		1.18±0.16		1.36±0.03		1.62±0.12
Malmo	fallow	1	0-15	1.05	15-30	1.29	30-60	1.53
		2		1.03		1.24		1.55
		3		0.96		1.09		1.50
		Mean[1]		1.01±0.05		1.21±0.10		1.53±0.03
Malmo	stubble	1	0-15	1.02	15-30	0.99	30-60	1.51
		2		0.96		1.04		1.44
		3		0.96		1.11		1.49
		Mean[1]		0.98±0.03		1.05±0.06		1.48±0.04
Navarre	fallow	1	0-15	0.94	15-30	1.65	30-60	1.67
		2		0.94		1.42		1.44
		3		0.94		1.56		1.58
		Mean[1]		0.94±0.00		1.54±0.12		1.56±0.12
Navarre	stubble	1	0-15	0.92	15-30	1.53	30-60	1.68
		2		1.16		1.56		1.44
		3		0.96		1.46		1.45
		Mean[1]		1.01±0.13		1.52±0.05		1.52±0.14

[1] Means reported ± standard deviation.

APPENDIX C: Table 3. Bulk density of soils used in Experiment 1980B.

Soil series	Treatment	Rep No.	Depth (cm)	Db (g/cm^3)	Depth (cm)	Db (g/cm^3)	Depth (cm)	Db (gcm^3)
Breton	fallow	1	0-13	0.82	13-30	1.51	30-60	1.61
		2		0.78		1.58		1.58
		3		0.87		1.43		1.58
		4		0.90		1.56		1.57
		5		0.76		1.61		1.62
		6		0.81		1.40		1.65
		Mean[1]		0.82±0.05		1.52±0.08		1.60±0.03
Breton	stubble	1	0-13	0.83	13-30	1.49	30-60	1.54
		2		0.89		1.52		1.54
		3		0.75		1.41		1.60
		4		0.76		1.43		1.55
		5		0.81		1.47		1.57
		6		0.80		1.56		1.52
		Mean[1]		0.81±0.05		1.48±0.06		1.55±0.03
Malmo	fallow	1	0-13	0.78	13-30	1.13	30-60	1.34
		2		0.72		1.25		1.68
		3		0.89		1.32		1.82
		4		0.75		1.17		1.60
		5		0.78		1.11		1.34
		6		0.76		1.25		1.54
		Mean[1]		0.78±0.06		1.20±0.08		1.55±0.19
Malmo	stubble	1	0-13	0.69	13-30	1.13	30-60	1.37
		2		0.68		1.06		1.26
		3		0.68		0.95		1.48
		4		0.71		0.96		1.50
		5		0.66		1.02		1.60
		6		0.68		1.17		1.70
		Mean[1]		0.68±0.02		1.05±0.09		1.48±0.16

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[1] Means reported ± standard deviation.

APPENDIX C: Table 4. Moisture content at time of sampling Experiment 1980A.

Soil series	Treatment	Depth (cm)	Moisture content (mm)[1,2]			
			November	January	March	May
Breton	fallow	0-15	36± 1	63± 5	60± 7	30± 1
		15-30	52± 1	49± 3	53± 2	43± 1
		30-60	109± 2	106± 3	112± 0	95± 7
		0-60	197± 2	218± 9	225± 9	168± 7
Didsbury	fallow	0-15	53± 1	62± 8	58± 5	47± 4
		15-30	62± 3	68± 9	68± 5	59± 6
		30-60	108± 5	105± 6	113± 5	111± 3
		0-60	223± 7	235±19	239±13	217± 6
Didsbury	stubble	0-15	62± 2	102±14	71± 5	53± 4
		15-30	53± 0	59± 5	55± 4	47± 3
		30-60	95±25	97± 5	108± 8	95± 5
		0-60	210±23	253±22	232±16	195± 7
Malmo	fallow	0-15	58± 4	64±9	74± 6	39± 0
		15-30	54± 2	66± 7	63± 2	46± 1
		30-60	105±12	121± 3	116± 7	86± 5
		0-60	217±13	251±14	253± 3	171± 6
Malmo	stubble	0-15	62± 2	101± 9	109±11	38± 4
		15-30	61± 1	71± 2	68± 2	42± 3
		30-60	120± 5	129± 5	121± 9	102± 5
		0-60	243± 6	301± 4	298±14	182±11
Navarre	fallow	0-15	55± 1	85± 9	88±10	41± 2
		15-30	69± 5	79± 5	75± 6	55± 8
		30-60	128± 3	131± 5	145± 8	117± 0
		0-60	252± 3	295± 9	308±15	214± 9
Navarre	stubble	0-15	58± 0	85± 8	111±30	48± 1
		15-30	68± 4	72± 2	73± 6	62± 2
		30-60	148±12	150±10	152± 3	123± 5
		0-60	274± 9	307±10	336±29	233± 6

[1] Mean values reported ± standard deviation.

[2] Moisture content (mm) = % MC/100 x Db(g/cm^3) x density H$_2$O(cm^3/g) x depth (cm) x 10 mm/cm.

APPENDIX C: Table 5. Moisture content at time of sampling Experiment 1980B.

Soil series	Treatment	Depth (cm)	Moisture content (mm)[1],[2]			
			November	January	March	May
Breton	fallow	0-13	26± 1	50± 4	53± 5	23±1
		13-30	57± 3	103±15	98±18	52±5
		30-60	109± 4	134±27	115± 5	96±5
		0-60	192± 4	287±19	266±11	171±8
Breton	stubble	0-13	28± 2	46± 4	52± 2	24±1
		13-30	55± 3	91±10	103±20	53±8
		30-60	107± 4	116± 9	116± 9	102±9
		0-60	190± 5	253±14	271±22	179±9
Malmo	fallow	0-13	34± 1	50± 8	49± 6	24±1
		13-30	63± 7	69± 9	67± 6	45±4
		30-60	102±11	112±19	107±14	84±4
		0-60	199±10	231±16	223± 8	153±5
Malmo	stubble	0-13	36± 1	50± 5	54± 5	22±2
		13-30	66± 6	64± 4	75± 5	43±2
		30-60	120± 8	111± 8	120± 9	98±9
		0-60	222± 7	225± 5	249± 8	163±4

[1] Mean values reported ± standard deviation.
[2] Moisture content (mm) = % MC/100 x Db(g/cm^3) x density H_2O (cm^3/g) x depth (cm) x 10 mm/cm.

APPENDIX C: Table 6. Experiment 1981A, Moisture content at time of sampling (0-15 cm).

Soil series	December	January	March	May
		Moisture content (mm)[1 2]		
Breton	35±1	37±1	32±3	38±3
Malmo	43±1	46±0	45±4	46±3

[1] Values reported are mean of four replicates ± standard deviation.
[2] M.C.(mm) = % MC/100 x Db(g/cm^3) x density H_2O (cm^3/g) x depth (cm) x 10 mm/cm.

APPENDIX C: Table 7. Experiment 1981B, Moisture content at time of sampling (0-15 cm).

Soil series	Treatment	December	January	March	May
		Moisture content (mm)[1 2]			
Breton	amended	36±1	36±3	33±2	30±1
	non-amended	35±2	35±3	32±1	32±2
Malmo	amended	44±2	48±1	45±3	48±3
	non-amended	44±2	46±3	46±3	46±3

[1] Means are average of 4 replicates ± standard deviation.
[2] M.C.(mm) = % MC/100 x Db(g/cm^3) x density H_2O (cm^3/g) x depth (cm) x 10 mm/cm.